DIALYTIC METHODS FOR SAMPLE TREATMENT IN ION CHROMATOGRAPHY

by

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Submitted in fulfilment of the requirements

for the degree of

Doctor of Philosophy

Department of Chemistry

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Hobart, Australia

July, 1993

DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of a university or other institute of higher learning, except where due acknowledgment is made in the text.

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Date: 4/3/1993

ABSTRACT

This thesis presents the results of a systematic study of the parameters affecting dialysis procedures, including active (Donnan) dialysis and electrodialysis, for the pretreatment of alkaline samples prior to ion chromatographic analysis. A preliminary study of enrichment of inorganic anions using an "Elutrap" apparatus is also presented. Dialysis methods were investigated with a view to applying membrane-based clean-up procedures to the determination of trace levels of inorganic anions in various samples following sample treatment by hydroxide fusion.

Donnan dialysis was carried out by passing sodium hydroxide solutions containing inorganic anions through a cation-exchange hollow fibre immersed in a hydrogen ion donating medium. As the sample is passed through the lumen of the fibre, a dialysis reaction involving exchange of sodium ions in the sample with hydrogen ions from the surrounding medium occurs, resulting in total or partial neutralization of the sample. Several acid solutions including slurries of cation-exchange resins were evaluated on the basis of neutralization efficiency and penetration of the acid anion through the membrane. Cation-exchange resins in the hydrogen form slurried with 0.1 M octanesulfonic acid gave optimal performance and when the resin was stirred occasionally the total theoretical neutralization capacity of the resin was achieved.

The use of an "Elutrap" apparatus was shown in this study to be impractical for sample clean-up and enrichment of anions. However, factors affecting the migration rate of inorganic anions under applied DC potential have been elucidated. An electrodialysis process, which uses an electrical field to stimulate the migration of ions through the membrane, was studied for off-line neutralization of strongly alkaline samples. This method utilizes an electrodialysis cell comprising three compartments separated from each other by cation-exchange membranes. Experimental parameters, such as the magnitude of the applied current or power, the

type of cation-exchange membrane used and the design of the cell were studied. Under optimal conditions, recoveries of solute anions (Cl^-, Br^-, NO_3^-, HPO_4^{2-} and SO_4^{2-} in the range 3-10 μg/ml) from 1 M NaOH solution were close to quantitative except for fluoride and nitrite. It is suggested that low recoveries for these ions were due to the formation of neutral, protonated species within the membrane with subsequent loss by diffusion.

A flow-through electrodialysis device, in which the sample was allowed to flow during the dialysis process, was studied for the on-line pretreatment of strongly alkaline solutions. Variations of the shape of the sample compartments and the size of the electrodes were studied in order to optimize the flow-through cell design and to minimize the heat generated inside the cell. Quantitative recovery for fluoride ion could be achieved using a Neosepta CMS cation-exchange membrane and the ability to successfully treat samples containing fluoride represented an improvement over the off-line cell.

The on-line electrodialysis method has been successfully applied to the determination of inorganic anions in vegetation samples obtained from the vicinity of an aluminium smelter, following sample preparation by hydroxide fusion. This work demonstrated that when correctly applied, the method could be used on different sample types which have been traditionally difficult to analyse by ion chromatography.

ACKNOWLEDGEMENTS

During the three and a half years that it has taken to complete this thesis, many people both in University of New South Wales, where I spent the first two years of this work, and in University of Tasmania have contributed their time and support toward the completion of this project. I would like to express my sincere gratitude and appreciation to all those who have helped me along the way, and in particular the following people:

Paul Haddad, my supervisor, for the opportunity to pursue this project, his support, guidance and friendship over the years.

Ray Simons at the School of Physics, University of New South Wales, my co-supervisor, for his assistance and advice.

The staff members of the Department of Chemistry, University of Tasmania, especially Peter Dove and John Davis for their assistance in the construction of the flow-through electrodialysis device.

The staff members of the School of Chemistry, University of New South Wales, for their help that made this work possible.

My fellow "Chromatography group" research students both in UTas and in UNSW over the past few years: Andrew, Peter, Frank, Tony, Sarah, Christine, Jim, Ofelia, Tuti, Ada, Joselyn, Terry Flynn at the Centre for Chemical Analysis for their warm friendship and Simon for his help in generating the CE results.

Finally, I would like to thank my wife, Lisna, for her love, patience and understanding throughout the good and the bad times during our stay in Australia and my mother for her endless support and continuous encouragement for so many years. It is to them and my late father that I dedicate this thesis.

LIST OF PUBLICATIONS FROM THIS THESIS

1. Dialytic Clean-up of Alkaline Samples Prior to Ion Chromatographic Analysis.
   - Soehendra Laksana and Paul R. Haddad
   - *Journal of Chromatography*, 602 (1992) 57.

   (Work from Chapter Four of the Thesis)

2. Electrodialysis for Clean-up of Strongly Alkaline Samples in Ion Chromatography.
   - Paul R. Haddad, Soehendra Laksana and Ray G. Simons.
   - *Journal of Chromatography*, 640 (1993) 135.

   (Work from Chapter Six of the Thesis)

3. Ion Chromatography of Strongly Alkaline Samples.
   - Soehendra Laksana and Paul R. Haddad.
   - *Chemistry in Australia*, 59 (1992) 282.

   (Work from Chapter Six of the Thesis)

4. Ion Chromatographic Analysis of Alkaline Samples Using an On-line Electrodialysis Device.
   - Soehendra Laksana and Paul R. Haddad.
   - *Chemistry in Australia*, 60 (1993) 276.

   (Work from Chapter Seven of the Thesis)

5. On-line Pretreatment of Alkaline Samples Using a Flow-through Electrodialysis Device.
   - Soehendra Laksana, Paul R. Haddad and Ray G. Simons.
   - paper in preparation.

   (Work from Chapter Seven of the Thesis)

LIST OF PRESENTATIONS FROM THIS THESIS

1. Dialytic Methods for the Clean-up of Alkaline Sample Solutions Prior to Ion Chromatographic Analysis.
   - Soehendra Laksana and Paul R. Haddad.
   - A paper presented at International Ion Chromatography Symposium, October 1991, Denver, USA. Abstract no. 28.

   (Work from Chapter Four of the Thesis)

2. A Study of Dialysis Treatments for the Clean-up of Alkaline Sample Solutions Prior to Ion Chromatographic Analysis.
   - Soehendra Laksana and Paul R. Haddad
   - A poster presented at the 11th Australian Symposium on Analytical Chemistry, July 1991, Hobart, Australia. Abstract no. 134.

   (Work from Chapter Four of the Thesis)

3. Electrodialysis of Alkaline Samples Prior to Ion Chromatographic Analysis.
   - Soehendra Laksana and Paul R. Haddad.
   - A paper presented at International Ion Chromatography Symposium, September 1992, Linz, Austria. Abstract no. 3.

   (Work from Chapter Six of the Thesis)

4. On-line Pretreatment of Alkaline Samples Using a Flow-through Electrodialysis Device.
   - Soehendra Laksana, Paul R. Haddad and Ray G. Simons.
   - A paper will be presented at International Ion Chromatography Symposium, September 1993, Baltimore, USA.

   (Work from Chapter Seven of the Thesis)

5. Electrodialysis of Alkaline Samples Prior to Ion Chromatographic Analysis.
   - Paul R. Haddad, Soehendra Laksana and Ray G. Simons.
   - A paper will be presented at the 12th Australian Symposium on Analytical Chemistry, October 1993, Perth, Australia.

   (Work from Chapters Six and Seven of the Thesis)

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CHAPTER ONE

INTRODUCTION

In the last two decades, ion chromatography (IC) has become a major tool for the determination of ionic species in various kinds of matrices. Hardly any sample pretreatment, except filtration, is required in the majority of cases for minute quantities of analyte of interests. However, widespread use of IC has also made it obvious that in certain cases some sample pretreatment steps may be mandatory to ensure the ultimate success of the analysis. The main objectives of these steps are to selectively remove matrix interferences from the sample and to bring the analyte concentration within the linear dynamic range of the detection system. Despite the fact that IC offers a wide choice of separation and detection modes, samples with high ionic strength continue to present a problem when IC is applied to the determination of inorganic anions. Deleterious effects on column life and performance are often observed when such samples are injected directly onto the ion chromatograph. These samples produce highly distorted analyte peaks and severe baseline perturbations due to the effect of the sample on the equilibria existing in the IC system.

When the high ionic strength of the sample is caused by the presence of elevated levels of sodium hydroxide, simple neutralization of the sample is unsuitable because the resultant high level of the acid anion generally causes interference problems. It is sometimes possible to use a cation-exchange resin in the hydrogen form, operated either in batch or column modes, to perform the pH adjustment. The sodium ions in the sample are replaced with hydrogen ions from the cation-exchange resin and the process leads to the neutralization of the sample without concomitant introduction of an acid anion to the sample. The approach is simple and relatively

effective, but suffers from a number of drawbacks. The sample volume required is large and may change due to the uptake or release of solvent from the resin. Contamination of the sample by ions leached from the resin material and loss of sample components due to adsorption on the resin may also occur. An alternative approach for pretreatment of alkaline samples is Donnan dialysis using a suitable cation-exchange membrane. This process involves the exchange of sodium ions from the alkaline sample solution on one side of the membrane with hydrogen ions from a hydrogen ion donating medium (such as an acidic solution) on the other side, leading to neutralization of the sample. Careful choice of the hydrogen ion donating medium is necessary to ensure that the process does not lead to contamination of the sample. Donnan dialysis offers a fast and reliable process in terms of IC sample clean-up. Further refinement to the Donnan dialysis method can be achieved by applying an electrical field across the membrane in a process known as electrodialysis. The transfer of ions through the membrane is stimulated by the electrical field so that higher ionic strength samples can be neutralized than by Donnan dialysis alone.

Whilst the use of Donnan dialysis in IC for the achievement of both matrix normalization and sample preconcentration has been widely investigated, few examples of sample neutralization using this approach have been reported. There has been no attempt to systematically study the factors affecting the Donnan dialysis process for the neutralization of alkaline samples in IC. The use of electrodialysis in IC has also been very limited and no study has been reported on the use of this technique for pretreatment of alkaline samples prior to IC analysis.

This thesis describes the results of a systematic investigation of membrane dialysis procedures for pretreatment of alkaline solutions prior to their analysis by anion-exchange IC. Factors such as the cell design, selection of the cation-exchange membrane, selection of the hydrogen ion donating medium, dialysis conditions and

neutralization capacity of the device have been considered to ultimately establish optimal conditions for a fast and reliable clean-up procedure in the determination of inorganic anions present in various samples prepared by alkaline fusion.

Chapter two gives a short review of the separation and detection methods generally employed in IC. Membrane-based dialysis processes, together with the classification of membranes used in each technique are also reviewed in this chapter as part of sample clean-up methods in IC. Chapter three is concerned with the description of the chromatographic instrumentation and apparatus employed throughout this work. General laboratory procedures and a list of chemicals used are also included. An additional experimental section precedes each chapter and outlines the experimental details relevant to the specific work discussed in that chapter.

Chapter four outlines a systematic study of the Donnan dialysis method applied to the neutralization of sodium hydroxide samples containing small quantities of inorganic anions prior to IC analysis. Membrane-based devices were constructed which use a cation-exchange membrane fibre immersed in a hydrogen ion donating medium. Several hydrogen ion donating media, including slurries of cation-exchange resins, were evaluated on the basis of their neutralization efficiency and penetration of the acid anion through the membrane.

The result of a preliminary study of sample clean-up and anion enrichment using an "Elutrap" apparatus is given in Chapter five. This study was carried out by applying constant potential to a mixture of inorganic anions in water. Factors which influenced migration of the inorganic anions through the apparatus were investigated. Chapter six describes the use of an electrodialysis method for off-line neutralization of strongly hydroxide samples containing trace levels of common inorganic anions. The process used an electrodialysis cell comprising three compartments separated by a stack of two planar cation-exchange membranes.

Experimental parameters, such as the magnitude of applied electrical fields, the types of cation-exchange membranes and the design of the cell were investigated in order to obtain optimum conditions for the process.

The extension of the off-line electrodialysis device into a flow-through cell for on-line pretreatment of strongly alkaline solutions is presented in Chapter seven. This chapter also discusses the use of the electrodialysis process on real samples by applying the technique to the analysis of vegetation and dust samples from the aluminium industry, following sample preparation by hydroxide fusion.

An overview and conclusions of the study are given in Chapter eight. This chapter highlights the advantages of dialysis techniques for matrix neutralization as part of sample pretreatment methods in the determination of inorganic anions by IC. It also illustrates that when correctly applied, the electrodialysis process allows the analysis of various samples which have traditionally proved difficult for IC.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Ion-exchange methods have long been used for separating and analysing mixtures of inorganic ions and for removing ions that interfere in quantitative analytical procedures [1, 2]. Such processes were usually discontinuous as fractions of column effluent needed to be collected and subjected to further analytical techniques such as titrimetry [3], fluorometry [4], spectrophotometry [5, 6], amperometry [7] and potentiometry [8]. The whole process lacked the speed and automation that is now expected in analytical procedures.

High performance ion-exchange separations of ions were attained by using relatively small bore columns containing a packing of uniform and small particle size, a constant eluent flow, and by using continuous detection of the separated sample components [9]. However, the separation of inorganic ions was still limited in spite of these developments. Most of the separation and detection systems employed for analysis of inorganic ions suffered from the limitations of being specific for a particular type of sample ion, from having a long analysis time, or being insensitive.

In 1975 Small, Stevens and Bauman published a novel ion-exchange chromatographic method for the separation and conductometric detection of ionic species [10]. The method combined a low-capacity anion-exchange column for separating the solute anions in series with a second ion-exchange column (a stripper column or a suppressor) for reducing the background conductance of the eluent and enhancing the signals of the eluted ions. This technique has enabled a rapid

determination of most common inorganic ions at low concentrations and has been accepted widely. The term "ion chromatography" was then introduced when the technique was licensed to the Dionex Corporation for commercial development.

Later developments in 1979 by Gjerde, Fritz and Schmuckler showed that ion chromatographic separation and conductometric detection of inorganic ions could be performed without the use of a suppressor unit [11]. This approach used an ion-exchange resin having a very low ion-exchange capacity which required only a very low ionic strength eluent and consequently enabled the use of conductivity detection without a suppressor column. Since then, the applications of ion chromatography (IC) with many combinations of separation and detection methods have broadened and today the term "ion chromatography" applies to virtually any high performance liquid chromatographic determination of ionic species.

Successful separation and detection of analytes in ion chromatographic analysis is often determined by the sample preparation step, which comprises collection, dissolution and clean-up procedures. With proper sample preparation, interfering materials can be eliminated from the sample prior to injection onto the ion chromatograph. Although there are different kinds of sensitive detectors, appropriate eluents, different types of separation modes, columns and packing materials, it must be realized that the sample clean-up step contributes significantly to the overall performance of the analysis, such that sample clean-up often determines the ultimate success of the analysis.

This chapter reviews the separation and detection methods that are now commonly employed in ion chromatographic analysis of inorganic anions. This is followed by a review of sample clean-up methods and the role of dialysis techniques in this process.

2.2 SEPARATION METHODS

2.2.1 INTRODUCTION

Separation methods in ion chromatographic analysis of inorganic anions can be classified as shown in Fig. 2.1. The main separation method is anion-exchange, which can be divided into suppressed and non-suppressed methods. The first uses a suppressor to reduce the background conductance of eluent whilst the second, non-suppressed method, does not. Other separation methods include ion-interaction chromatography and ion-exclusion chromatography, together with some miscellaneous methods that cannot be defined accurately as IC but can be employed for the same samples as those usually encountered in IC [12, 13, 14].

2.2.2 ANION-EXCHANGE METHODS

2.2.2.1 Suppressed ion chromatography

As described previously, this method is based on a combination of an anion-exchange column and a suppressor unit, coupled with the conductometric determination of separated ions [10]. The schematic hardware configuration of the system is shown in Fig. 2.2. For anion determinations the system employs salts of weak acids, such as dilute carbonate/bicarbonate buffer, to separate the sample anions on an anion-exchange column of moderate to low capacity. The eluent flows through the suppressor unit and is converted into a weakly conducting weak acid by the regenerant, whilst at the same time the sample anions are converted to highly conducting acids. The net effect is a highly conducting acid solute band eluted in a weakly conducting weak acid background [15].

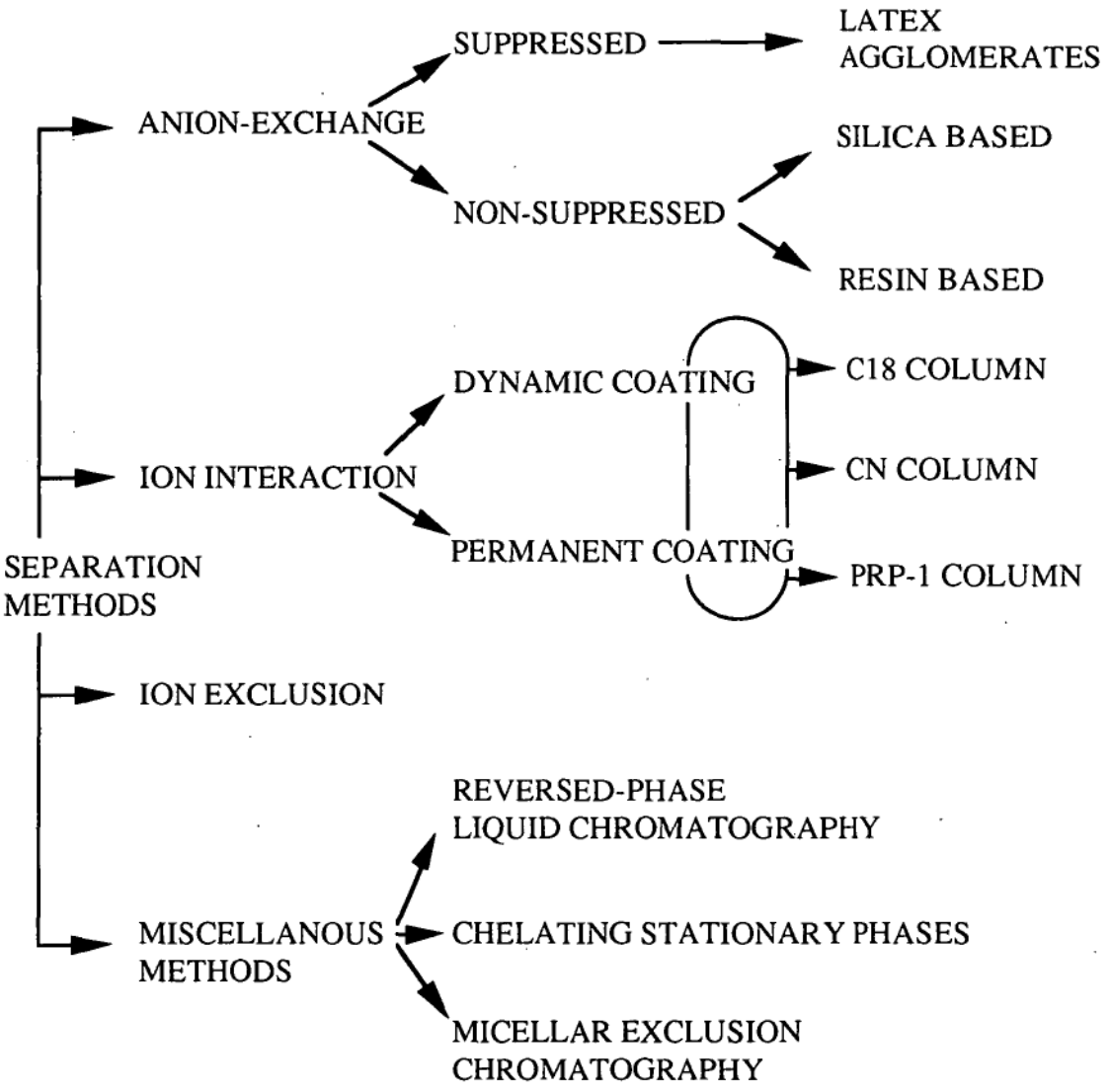


Fig. 2.1 Classification of separation methods used for inorganic anions.

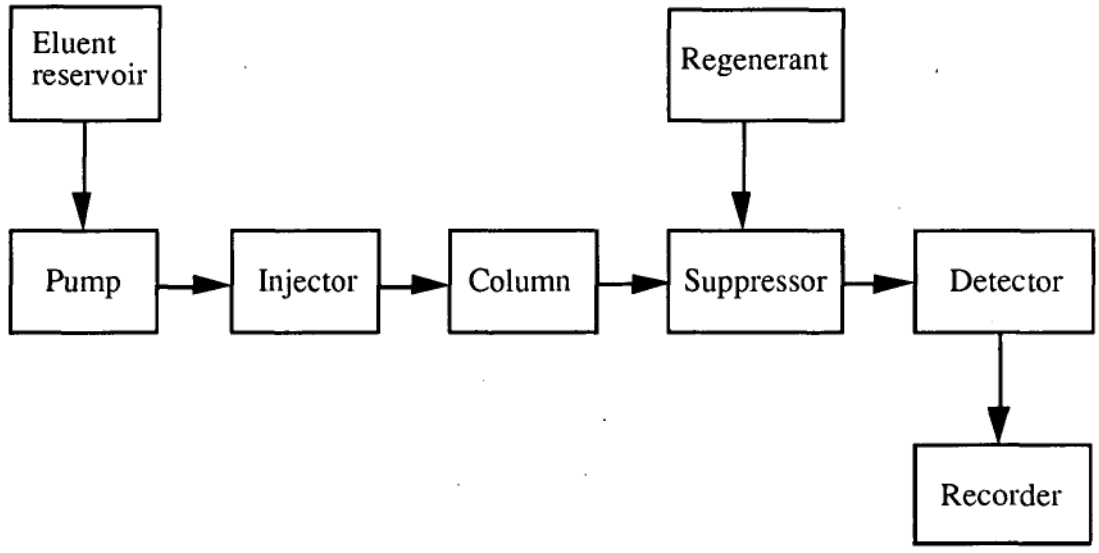


Fig. 2.2 Instrumentation for suppressed ion chromatography.

The anion-exchange column in the suppressed system is packed with an agglomerated ion-exchange resin. This resin consists of a styrenedivinylbenzene copolymeric core (10-30 μm) with its outer shell reacted to form a thin layer of sulfonic acid groups. The sulfonated resin is then converted into an anion-exchange by treatment with fine polymer (latex) particles having quaternary ammonium anion-exchange sites. The latex particles (in the size range 20-100 nm) attach themselves by electrostatic attraction to the resin surface to form a thin layer surrounding the core of the bead. The final resin product consists of layers comprising the inner core, the sulfonated layer and the layer of anion-exchange particles [16, 17].

The agglomerated anion-exchange resin can be produced by pumping a suspension of aminated latex through a column packed with sulfonated core particles until an excess emerges [18]. Alternatively, the two components may be mixed to form a precipitated agglomerate which is then used to pack the column in the conventional manner. The first approach is considered to be the best method for preparing the column as it produces more efficient columns, provided column plugging with the latex suspension can be avoided. The presence of a polyvalent salt solution has been found to be a necessity in performing the agglomeration step in order to obtain a dense and uniform agglomerate [19].

The advantage of agglomerated anion-exchange resins over conventional ion-exchange resins is their chromatographic efficiency [20]. Efficient separations are possible due to the existence of short diffusion paths, leading to a faster mass-transfer characteristics. Compared to other pellicular resins having a silica or glass core, the agglomerated resin is extremely stable even when strongly alkaline eluents are used. The resin is also mechanically stable, allowing high flow-rates to be used so that short analysis times can be obtained. However, these resins are susceptible to some organic solvents which may cause mechanical failure of the agglomerated resin beads.

Although the anion-exchange material on the resin is of high capacity, the overall ion-exchange capacity of the resin is quite low and is typically in the range of 0.02 to 0.05 meq/g. The selectivity of agglomerated resins is comparable to that of a conventional high capacity resin in which the anion-exchange functional group is bonded chemically to the surface of the resin. Selectivity is influenced mainly by the nature of the functional group on the latex and to a lesser extent by the chemical natures of the core and latex particles or by the degree of cross-linking [20].

The earliest work on suppressed IC employed a suppressor column that contained macroporous strongly acidic cation-exchange resins. This column was used to protonate the carbonate/bicarbonate buffers generally used as the eluents for anion separations. The reactions which take place in such a suppressor column using this eluent, and considering the case of chloride ions as solutes, are outlined below.

$$\text{Resin-H}^+ + \text{Na}^+\text{HCO}_3^- \leftrightharpoons \text{Resin-Na}^+ + \text{H}_2\text{CO}_3 \quad (1)$$

$$\text{Resin-H}^+ + \text{Na}^+ + \text{Cl}^- \leftrightharpoons \text{Resin-Na}^+ + \text{H}^+ + \text{Cl}^- \quad (2)$$

The overall result of these processes is that the eluent conductance is decreased greatly, whilst the conductance of the sample is increased by virtue of the replacement of sodium ions with hydrogen ions. In a typical case, the background conductivity is lowered from 700 μScm^{-1} to 23 μScm^{-1} and the analyte signal enhances by a factor of 16 [16].

A suppressor column filled with strongly acidic cation-exchange resin could be used only until all of the active sites were converted into the sodium form. The suppressor therefore needed to be regenerated periodically by passing a strong acid solution such as 0.25 N H_2SO_4 solution through the column. However, the degree of exhaustion of the column was found to affect the analytical response to solute peaks and significant band broadening of the peaks occurred as a result of the additional

dead volume introduced by the suppressor column [21]. Besides the conversion of eluent and sample anions into their acid forms, other phenomena were found to occur in the suppressor. Anions of strong acids will form highly ionized species and may show variable retention in the suppressor column due to ion-exclusion effects. Typically only anions whose conjugate acid has a pKa < 7 can be determined. This excludes many important anionic species such as borate, carbonate and cyanide [22].

Some of the limitations of column suppressors were eliminated through the use of the hollow cation-exchange fibre suppressor introduced in 1981 by Stevens *et al.* [23]. The eluent is passed through the interior of the fibre, whilst a suitable regenerant solution passes over the exterior of the fibre, usually in a counter-current direction. Eluent anions cannot permeate the fibre wall due to Donnan exclusion forces but cations are exchanged and the eluent is suppressed in the same manner as when using packed-bed suppressor columns. Sulfuric acid solution is usually used as the regenerant solution and is converted to sodium sulfate. However, sulfate ions may enter the eluent stream (despite the fact that this is forbidden by Donnan ion-exclusion phenomena) when using sulfuric acid as the regenerant, especially when the concentration is high. It has been demonstrated that large ions have a smaller penetration rate through the membrane, so that dodecylbenzenesulfonic acid is a useful regenerating solution for the hollow fibre suppressor, especially when concentrated eluents are used [24, 25].

The earliest hollow fibre suppressors were limited in efficiency and sometimes gave incomplete protonation (suppression) of the eluent due to the use of high eluent flow-rates or high eluent concentration. The suppressor also contained considerable dead volume which resulted in broadening of sample peaks. Attention was therefore focused on improving mass transfer to the fibre wall and at the same time lowering the void volume of the suppressor. A sufficient mass transfer of ions can be achieved by introducing turbulence or by reducing the cross section diffusion path

length of the ions [26, 27]; for example by inserting a nylon filament into the hollow fibre or by packing the fibre with polystyrene beads [28]. Insertion of a nylon filament permits coiling the hollow fibre into a helix and induces fluid turbulence which consequently increases ion transport to the fibre wall [29]. The use of beads which are arranged in a zig-zag pattern inside the hollow fibre reduces the dead volume inside the suppressor and also induces turbulent flow.

Different approaches to increasing the suppression efficiency of the packed-bead suppressor have been discussed in some detail by Dasgupta [30]. These have included replacing the inert beads with ion-exchange resin beads, packing beads around the exterior of the fibre to provide mechanical support, altering the shape of the packing beads and application of an ultrasonic field to the system. Despite all these developments, hollow fibre suppressors still have a limitation due to the use of fibres with small internal diameters, leading to low ion-exchange capacity and therefore a restriction in the eluent concentrations usable with the device.

A more recent design, the micromembrane suppressor, appears to be quite efficient and is able to provide a higher ion-exchange capacity suitable for most IC eluents. The micromembrane suppressor is a dual membrane device constructed of two membrane sheets with regenerant flow on both sides of the unit. The eluent passes through a central chamber which has ion-exchange membrane sheets as the upper and lower surfaces. Regenerant flows in a counter-current direction over the outer surfaces of both of these membranes. The surface available for exchange processes is thereby increased greatly in comparison to fibre suppressors, and so is the ion-exchange capacity. The high dynamic capacity of the micromembrane suppressor allows continuous suppression of concentrated eluents, such as 0.1 M NaOH, to a background conductivity of less than 20 μS. The micromembrane suppressor combines the advantages of other suppression devices and at the same time, eliminates their drawbacks [31, 32]. A more efficient micromembrane suppressor

using an electrical field to enhance the transfer of ions across the membrane has been suggested [33] and a flow-through type of electrochemical membrane suppressor has also been reported [34] in attempts to maximize the performance of suppressed ion chromatographic method. The background conductance of the eluent may be lowered further by inserting a post suppression device between the suppressor and the detector. The post suppression device is used to remove H_2CO_3 from the suppressed eluent, and this is achieved by passing the suppressed eluent through a CO_2 permeable tubing, such as PTFE tubing [35], silicone rubber tubing [36] or porous polymer tubing [37].

2.2.2.2 Non-suppressed ion chromatography

The growth of suppressed IC was accompanied by the simultaneous development of an alternative chromatographic method which did not require the use of a suppressor column and was compatible with conventional HPLC equipment. This method, known as non-suppressed or single column IC, was introduced in 1979 by Fritz and co-workers [11, 38]. The technique enabled determination of anions using conventional HPLC equipment since the analytical column could be linked directly to the conductivity detector without the use of a suppressor. This was possible through the use of an analytical column containing an ion-exchange resin material with very low ion-exchange capacity (usually 7 to 40 μeq/g). Hence, only eluents of a very low ionic strength were required for solute elution and a very low background conductance was produced. Eluents comprising dilute solutions of aromatic acids, such as benzoate, phthalate or sulfobenzoate, were used because of their high affinity with the ion-exchange sites and low background conductance.

The original resins prepared by Fritz and co-workers were chloromethylated polystyrene beads which were aminated to produce strong base anion-exchange resins with good stability [39], but the efficiencies of the resins were low and

resulted in poor chromatographic separations. This prompted efforts to design high efficiency resin-based anion-exchange materials, so that the anion-exchange columns which are now available commercially have high efficiencies (12000-25000 theoretical plates/m) and low ion-exchange capacities (30-200 μeq/g). These columns use a variety of different resin substrates including polystyrene-divinylbenzene [40], polymethacrylate gel [41] and other hydrophilic macroporous polymers [42] to which the ion-exchange functional groups are bonded. These materials are tolerant toward eluents and samples with extreme pH values, so that the range of ions that can be analysed is extended. However, the use of polymeric resin as the substrate in an anion-exchange column introduces a pressure limitation and a restriction on the permissible percentage of organic modifier in the eluent.

Silica-based anion-exchange materials were developed concurrently with the resin-based materials with the aim of producing high efficiency low capacity anion-exchange materials. These can be divided into two distinct groups. The first comprises polymer-coated materials which are prepared by coating a layer of polymer, such as polystyrene, silicone or fluorocarbon onto a silica particle, followed by derivatization of this layer to introduce anion-exchange functional groups. The second comprises functionalized silica materials where a functional group, such as a quaternary ammonium group, is chemically bonded directly to a silica particle.

Silica-based anion-exchange columns have chromatographic efficiencies which are typically in the range of 16000-25000 theoretical plates/m [43, 44] and have small particle size to produce uniform and stable chromatographic beds which are not subject to stringent pressure or flow-rate limitations [45, 46]. Silica packing materials also have a high tolerance to organic modifiers [41] which enables manipulation of ion-exchange selectivities or reduction in column fouling through the use of organic modifiers as eluent components. The retention mechanism of a silica-based material is often simpler than for other materials because of the low

probability of secondary interactions between solute ions and the silica substrate [47]. This means that retention times are often shorter on silica columns than on other packings having similar ion-exchange capacities.

Several disadvantages also exist with the use of silica-based anion-exchange columns. The working pH range is restricted to 2-6.5; lower pH may cause a loss of ion-exchange capacity due to cleavage of the functional groups, whilst alkaline pH values may dissolve the silica matrix itself [39]. The columns have a small linear range of sample loading and some metal ions are retained on the column and may be eluted as interferences in an anion separation [48].

The introduction of non-suppressed IC has stimulated the use of detection methods other than conductivity. This development has also led to the introduction of a variety of eluents which has resulted in a wide range of separations for many different anions. The most commonly employed eluents are salts of carboxylic and sulfonic acids, as these generally have low limiting equivalent ionic conductance. Some typical eluent species include aromatic carboxylic acids such as benzoic acid, phthalic acid and p-hydroxybenzoic acid and these are suitable for use with indirect detection modes. Aliphatic sulfonic acids such as methanesulfonic acid and heptanesulfonic acid have been used as eluents with direct UV detection. A number of studies have been reported in evaluating the suitability of eluents for the non-suppressed technique [39, 49-59], while gluconate/borate buffer has been found to give excellent separations of univalent and divalent anions. The greater variety of eluents, columns and detection modes that can be used with non-suppressed IC has now made the technique as widely used as suppressed IC.

2.2.3 ION-INTERACTION METHODS

Ion-interaction chromatography is also known such as ion pair chromatography [60],

paired ion chromatography [61], dynamic ion-exchange chromatography [62] and hetaeric chromatography [63]. The technique is an extension of conventional reversed-phase chromatography and involves the addition of an oppositely charged, hydrophobic reagent (called the ion-interaction reagent or IIR) to the mobile phase in order to obtain separation of ionic solutes.

The retention mechanism of ion-interaction chromatography has been the focus of a large volume of literature and three models have been suggested to describe the mechanism, each being based on the establishment of a different equilibrium. The first is the ion-pair model where an ion-pair is envisaged to form between the solute ion and the hydrophobic IIR. This occurs in the aqueous-organic eluent and the resultant neutral ion-pair interacts with the stationary phase as a result of solvophobic forces [63, 64]. The second model, dynamic ion-exchange, proposes that a dynamic equilibrium is established by the adsorption of IIR onto the stationary phase. The stationary phase is then envisaged to behave as an ion-exchanger for the solute ions [65-68]. The third mechanism is the ion-interaction model which is viewed as intermediate between the two previous models [69-71]. The cationic hydrophobic IIR is adsorbed onto the stationary phase forming a primary layer while the co-anion occupies a diffuse secondary layer. This results in the formation of an electrical double layer at the stationary surface.

Ion-interaction chromatography has been performed successfully on a wide range of columns including silica-based reversed-phase columns [65-68, 72-76], neutral polystyrenedivinylbenzene columns [61, 68, 75, 77] and the more polar cyano columns [78, 79]. The choice of column is usually based on such considerations as chromatographic efficiency, pH stability and particle size rather than on differences in chromatographic selectivity.

The most important component in eluents for ion-interaction chromatography is the

IIR itself. The IIR usually has to meet some requirements such as compatibility with other eluent components or with the desired detection system, ability to adsorb onto the stationary phase and possession of an appropriate charge which is unaffected by eluent pH [14]. The IIR can coat the stationary phase in two distinct ways, leading to 'dynamic' or 'permanent' coating. Dynamic coatings are obtained by maintaining a moderately hydrophobic IIR, such as tetrabutylammonium salts, in the eluent at a constant concentration. Permanent coatings are produced when more hydrophobic IIRs, such as cetylpyridinium salts, are used. In this approach the IIR is removed from the mobile phase after the column has been initially conditioned.

Ion-interaction chromatography is now a well-established alternative to ion-exchange as a separation method. The technique has an advantage in that a greater number of mobile phase parameters can be manipulated to control the retention of solute ions. These include concentration and type of IIR, organic modifier content, counter-ion concentration and pH. Further advantages of the method are the flexibility it offers for the adjustment of the ion-exchange capacity of the columns [39] and the fact that it also enables the use of conventional HPLC equipment to perform anion analysis.

2.2.4 ION-EXCLUSION METHODS

Ion-exclusion chromatography involves the use of a resin-based column for the separation of ionic solutes from weakly ionized or neutral solutes. The technique is also known by a variety of names, such as ion-exclusion partition chromatography [80], Donnan exclusion chromatography [81], ion chromatography exclusion [82] and ion-moderated partition chromatography [83]. The solute ions are separated by the exclusion of ions from the resin and by partitioning of ions between the solvent in the mobile phase and that within the resin. Strong and weak acid anions are separated on a cation-exchange column. Strong inorganic acid anions, such as chloride and nitrate, are repelled by the negative sulfonic acid groups on the resin

and hence are excluded from the resin and eluted at the void volume of the column. Weak acids, such as acetic and formic acid, exist mostly in the protonated or molecular form and are not excluded from the resin. They are delayed in their passage through the resin by a combination of partitioning effects and van der Waals forces which result in significant retention times [84].

The column is usually packed with functionalized polystyrenedivinylbenzene polymers of greater ion-exchange capacity than those of packings used for ion-exchange separation method. This is required so that the number of functional groups on the resin is sufficient to exert an appropriate Donnan exclusion effect. The size of the column is usually larger than a conventional IC column because a considerable volume of resin material is necessary to provide sufficient occluded liquid phase to permit the separation of solutes of similar size and charge. Improvement in polymeric packing materials [85, 86] has allowed the technique to be applied to the separation of organic acids [86-91], weak inorganic acid anions [92-96] and polar organic compounds such as alcohols and carbohydrates [83, 90, 97].

Early work on ion-exclusion chromatography employed water as an eluent [98, 99] and it was observed that strong acids were completely excluded, whilst weaker acids permeated selectively into the resin and their retention times were proportional to their pKa values. The use of water as an eluent is limited by poor peak shape of the retained solutes. This was improved by the use of acidic eluents which converted sample acids into their molecular form [100]. This also extended the use of the technique to separate relatively strong acids and bases by limiting their degree of ionization. Typical eluents which are now commonly employed are dilute mineral acid solutions, such as sulfuric acid, hydrochloric acid and also aliphatic sulfonic acid solutions. UV detection is usually employed when sulfuric acid is used as the eluent [85, 86]. Conductivity detection is often employed with hydrochloric acid eluent after the eluent is suppressed by a cation-exchange column in the silver form.

The suppressor column removes HCl from the eluent stream by exchanging H^+ for Ag^+ with subsequent precipitation of AgCl [101]. Conductivity detection without the use of a suppressor can be employed when aliphatic sulfonic acids are used, as these solutions give a relatively low conductance background.

Studies on the retention process in ion-exclusion chromatography [102-105] have shown that numerous factors play a part in the process and can be varied to alter the retention of solutes. These factors include ion-exchange capacity and degree of cross-linking of the stationary phase, degree of ionization and molecular size of the solute, organic modifier content, ionic strength and type of mobile phase counter-ion. Several applications of ion-exclusion chromatography include the determination of carboxylic acids, weakly ionized inorganic compounds, and water [14].

2.2.5 MISCELLANEOUS SEPARATION METHODS

In addition to the separation methods described earlier, a number of alternative approaches have been suggested. These include reversed-phase liquid chromatography, chelating stationary phases and micellar exclusion chromatography [14]. These techniques can be categorized as IC as they are also applicable to the same samples that are normally determined in IC.

Reversed-phase liquid chromatography with C_{18} columns has been used to separate metal ions after first complexing the metal ions with a suitable ligand. The metal complexes formed are uncharged and so permit the separation to be achieved on conventional reversed-phase columns. In most cases, sample preparation steps including solvent extraction, evaporation and redissolution are necessary prior to the chromatographic separation, since most of the chelates formed are water-insoluble. Some ligands which have been applied in HPLC separations of metal chelates include dithiocarbamates [106], 8-hydroxyquinoline [107, 108], β-diketones [109],

dialkyldithiophosphates [110, 111], xanthates [112] and hydrazones [113, 114]. Separation of organometallic compounds has also been accomplished by reversed-phase chromatography [115, 116] with the use of atomic spectroscopic detection methods. Examples are the separation of alkyllead, alkylmercury, alkylarsenic and alkyltin compounds. The addition of buffer to the mobile phase in order to suppress the ionization of analyte solutes has enabled the separation of weak acids and bases on a C_{18} column. The method is limited in that only buffers having pH values in the range 3-8 can be used. The reason for this is that the C_{18} stationary phases are unstable outside this pH range [71, 117].

Chelating stationary phases formed by immobilizing a ligand onto the stationary phase have been applied to the separation of metal ions, where the separation of solutes on the chelating stationary phase is manipulated by varying the eluent pH or through the addition of a competing ligand to the eluent. In each case, the ligand is chemically bound to a support material, such as styrenedivinylbenzene polymers or silica, using an appropriate reaction. Some examples of the ligands used are propylenediaminetetraacetate [118], β-diketones [119], hydroxamic acids [120], phenylhydrazones [121] and dithizone [122]. A recent development in the field of chelating stationary phases has been the use of crown ethers or cyclic polyethers as the ligand and this has been applied to the separation of a series of alkali metal salts and inorganic anions with water as eluent [123-126].

Micellar exclusion chromatography utilizes the formation of micelles by surfactant molecules in the eluent to improve the chromatographic selectivity [127, 128]. The micelles in the eluent are excluded from part of the stationary phase, whilst the solute ions partition between the micelle and the bulk solvent in the eluent, and also between the stationary phase and the eluent. The technique has been applied to the separation of inorganic anions and cations [129, 130]. The surfactants for anion separation include hexadecyltrimethylammonium chloride (HTAC) and

dodecyltrimethylammonium chloride (DTAC), whilst sodium dodecylsulfate (SDS) has been used for cation separation.

2.3 DETECTION METHODS

2.3.1 INTRODUCTION

Early IC studies utilized conductometric detection for the determination of anionic species but developments in separation methods have widened the range of alternative detection methods. Detection methods which can be employed in IC are classified according to the scheme shown in Fig. 2.3. Detection of eluted anions is always based on the difference in a measured property between the solute and eluent anions since a solute anion displaces an equivalent number of eluent anions from the mobile phase during elution. A detection method can be termed as a "direct" method when the eluent anion has a lower value of a measured property than the solute anion. An "indirect" method results when the eluent anion has a higher value of the measured property than the solute anion. Positive peaks result when a direct detection method is used, whilst indirect detection will produce negative peaks. Careful choice of detection method is therefore essential to ensure the ultimate success of analysis in IC. The detection method must be compatible with the sample ions and the eluent employed in the separation method.

2.3.2 CONDUCTIVITY DETECTION

Conductivity is the most widely employed detection method in IC because of its universal applicability (since all ions are electrically conducting) and because of its relative simplicity. In ion-exchange chromatography of a fully ionized solute, the change in conductance (ΔG) which accompanies the elution of a solute can be given

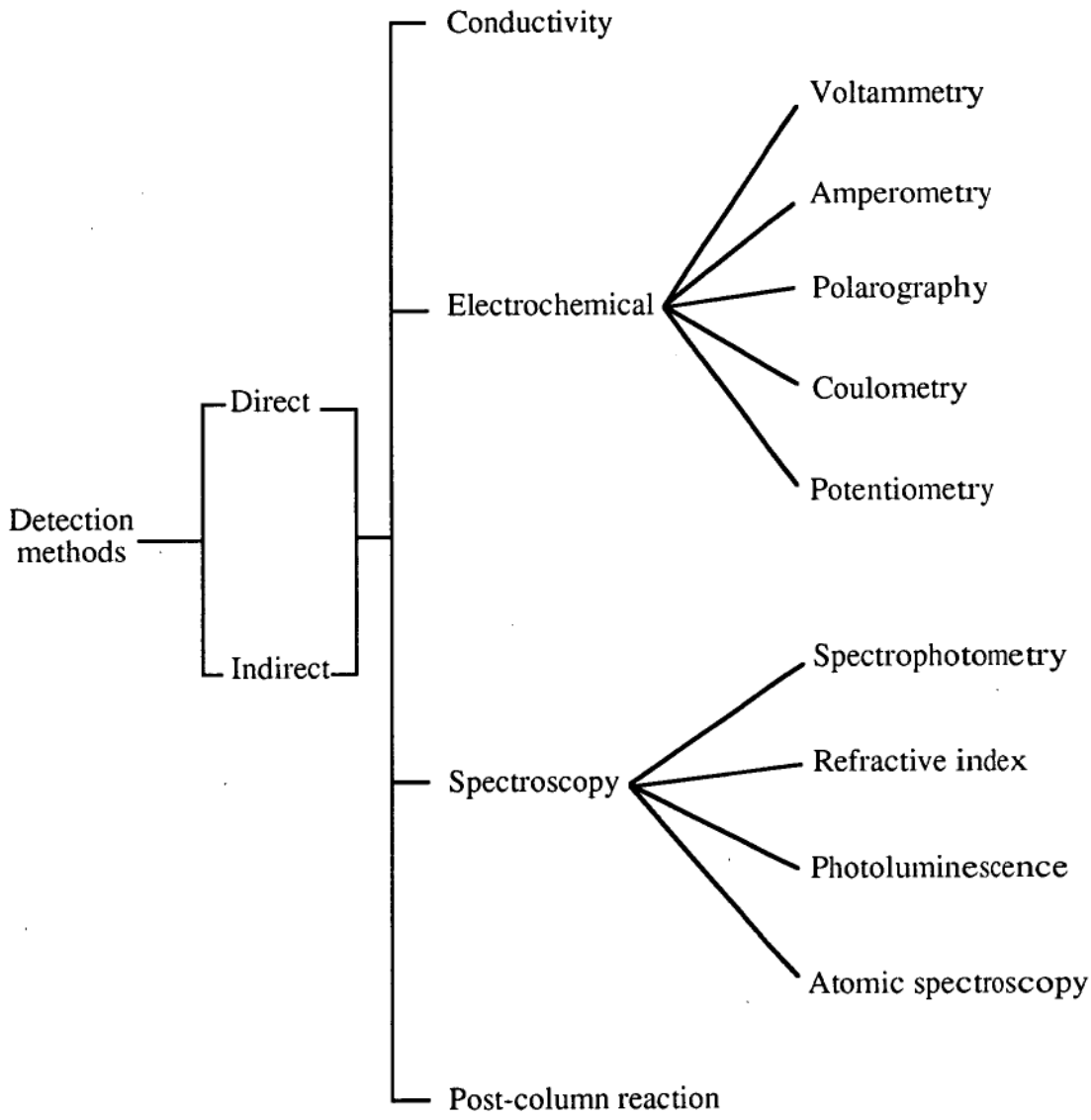


Fig. 2.3 Detection methods used for ion chromatography.

by the following equation :

$$\Delta G = \frac{(\lambda_{S^-} - \lambda_{E^-})\, Cs}{10^{-3}\, K}$$

The signal observed is proportional to the solute concentration (Cs) and to the difference in limiting equivalent ionic conductances between the eluent (λ_{E^-}) and solute ions (λ_{S^-}) [131]. This equation clearly shows that the bigger the difference between the limiting equivalent ionic conductances of the solute and eluent ions, the more sensitive is the conductivity detection. The difference in conductances mentioned above can be maximized by two different approaches. The first approach is to select an eluent of very low limiting equivalent ionic conductance, such as benzoate or phthalate [11, 38], or by suppressing the background conductivity of the eluent before it reaches the detector. The second approach is to select an eluent anion with a very high limiting equivalent ionic conductance, such as potassium hydroxide, and to monitor the decrease in conductance on elution of a solute ion [50]. The use of a hydroxide eluent has enabled the separation of weak acid anions such as silicate, cyanide, acetate, formate and arsenite on an anion-exchange column since these species are fully ionized at the high pH of the eluent [50, 132-134].

The increased use of conductivity detection has prompted a great deal of research into improvements in detector design and performance. Most conductivity detectors operate according to the Wheatstone bridge principle [135] and several problems in balancing such a bridge circuit have arisen from phenomena occurring within the cell itself. Temperature fluctuations have also been shown to affect both the sensitivity and reproducibility of conductivity detection [62, 136, 137], since the temperature coefficient for conductivity measurements is approximately 2% / ^{0}C [138].

The conductivity cell generally consists of a small chamber (approximately 3 µl) with two electrodes [139], although some commercial instruments use up to five electrodes [140]. Conductivity cells with internal volume of less than 0.5 µl have also been reported for use with microcolumn IC [141, 142]. Some cell designs use a bi-polar pulse technique to measure rapidly changing conductance [143, 144] and a dual-cell differential conductivity detector has been used to minimize baseline drift [145] and to allow simultaneous determination of both anions and cations. Commercially available conductivity detectors provide excellent thermal stability with wide linear ranges and can be operated at very low sensitivity, giving detection limits in the order of 100-500 ppb for most anions [39].

2.3.3. ELECTROCHEMICAL DETECTION

Detection techniques which involve the application of an electric potential to a sample solution, followed by measurement of the resultant current, can be defined as electrochemical methods. The common characteristic of these techniques is that a chemical reaction (e.g. Faradaic oxidation or reduction) occurs during the measurement. These techniques include voltammetry, amperometry, polarography, coulometry and potentiometry.

Voltammetric detection has limited applicability in IC since only electroactive species can be monitored by this method. However, the selectivity of voltammetric detectors can be exploited in cases where inadequate separation occurs or interferences are a problem. They are often used in tandem with other detectors to aid in peak identification or in speciation studies [74, 146, 147].

Amperometric detection is usually employed in the determination of anions which readily undergo oxidation reactions at relatively low potentials, such as CN^-, SCN^-, Br^-, I^-, NO_2^-, $C_2O_4^-$, S_2^- and HSO_3^- [94, 147, 148]. The optimal oxidation potential

of the anion must be chosen carefully to ensure the successful application of amperometric detection. The values for such potentials under different experimental conditions are available in the literature [149]. Alternatively, voltage-current curve (voltammograms) can be constructed under either static or dynamic conditions [150, 151].

The application of amperometric detection using a dropping mercury electrode (i.e. polarography) is possible with IC. However, the difficulty of constructing low-volume cells containing the dropping mercury electrode has limited the use of this approach [152]. On the other hand, coulometric detection requires a large electrode surface area to achieve complete electrolysis of the solute and therefore a larger cell volume is required. Coulometric cells are often difficult to dismantle and maintain, are sometimes expensive and can be applied only to a limited range of working electrode materials. For these reasons, the use of this approach in IC has been limited.

Potentiometric detection involves the measurement of the potential of an indicator electrode with respect to a reference electrode under conditions of minimal or zero current [153]. The potential of the indicator electrode varies with the concentration of the ion in the solution in accordance with the Nernst equation. Indicator electrodes which have been used include ion selective electrodes and copper wire electrodes. The technique has been applied widely to the determination of ionic species in aqueous solution, but the use of potentiometric detection in IC is limited by the moderate sensitivity of the technique.

2.3.4 SPECTROSCOPIC DETECTION

Spectroscopic detection methods are commonly employed in IC and are second only to conductivity detection in their frequency of usage. Most spectroscopic detection

methods can operate in a direct or indirect mode and include UV/Vis spectrophotometry, refractive index measurements, fluorescence and atomic spectroscopy.

Direct UV absorption detection has been used widely for the determination of anionic solutes in IC. This is due to the fact that a considerable number of anions, such as NO_2^-, NO_3^-, Br^-, MoO_4^{2-}, I^-, IO_3^- and BrO_3, show appreciable UV absorbance in the 175-220 nm range [154-157]. Other common anions, such as F^-, Cl^-, SO_4^{2-} and HPO_4^{2-}, do not show significant UV absorbance which allows for some degree of detection selectivity. The method has proved particularly useful for the determination of UV absorbing anions (nitrite and nitrate) in the presence of high chloride levels [146].

An obvious requirement in direct UV measurement is that the eluent composition must be optically transparent at the detection wavelength employed to allow sensitive determination of anionic species. For this reason, eluents such as phosphate buffer [78, 79], bicarbonate buffer [155, 158], sulfate [159], alkyl sulfonate [146, 156] and chloride [66] have been used. Detection limits obtained using this method vary depending upon the molar absorptivity of the solute anion and the background absorbance of the mobile phase, but they are generally in the order of 20-100 ppb for most anions [155].

Indirect UV absorption has become a popular method for the determination of inorganic anions. This development can be related directly to a rapid increase in the use of eluents containing aromatic acids, such as phthalate, benzoate, sulphobenzoate and benzenetricarboxylate [160, 161], in anion-exchange methods employing conductivity detection. The method can be more flexible than conductivity detection since it can be used in conjunction with higher capacity ion-exchange columns and higher strength eluents. Indirect UV detection has been the subject of many studies,

which include the criteria for eluent selection [162], performance optimization [163], modelling of analyte response [164, 165] and the quantitation of solutes without the use of standards [166]. This approach has also been used to eliminate the response to selected solute peaks [167, 168] and for simultaneous detection of cations and anions [169].

Direct refractive index (RI) measurement is not particularly viable with IC as most of solutions of inorganic anions have refractive indices similar to most potential eluent solutions. This mode of detection is not very sensitive and is usually employed only when other detection methods have been shown to be unsuitable. RI detection has been reported for AsO_2^- and AsO_4^{3-} [170]. On the other hand, indirect refractive index detection has been widely used for the detection of inorganic anions. The detection mode can be employed with the same eluents used with indirect spectrophotometric detection such as phthalate and benzoate [171]. This technique has been shown to have detection limits which are comparable to those obtained using indirect spectrophotometric detection or direct conductivity detection.

Direct fluorescence detection in IC is very limited in scope due to the fact that most of the solutes normally encountered in IC do not exhibit fluorescence. Indirect fluorescence detection potentially offers great sensitivity and has been applied in the determination of inorganic anions by a simple exchange mechanism between a fluorescent eluent ion and the eluted solute ion. Eluents such as salicylate [172, 173] have been shown to give a suitable level of background fluorescence and to exhibit appropriate elution characteristics.

Atomic spectroscopic methods are usually highly selective and have not been widely used for the determination of anions in IC. The main problem which emerges when an atomic spectroscopic instrument is coupled directly to the column effluent line of an ion chromatograph is the different flow-rates existing with each technique.

However, atomic absorption spectroscopy (AAS) has been used with IC for the determination of chromate [174] and for detection of arsenic species by hydride generation [175, 176]. Indirect detection of solute ions using AAS has also been reported using a lithium hollow-cathode lamp but a noisy baseline and moderate sensitivity resulted [177]. The selective flame emission detection of phosphorous- and sulphur-containing anionic species has been reported [178], and inductively coupled plasma atomic emission spectrometers have also been coupled to an ion chromatographic system to determine arsenic species [170, 176, 179]

2.3.5 POST-COLUMN REACTION DETECTION

Detection using post-column reaction (PCR) involves the addition of a colour forming reagent to the column effluent *via* a mixing apparatus, with the product usually being detected by UV/VIS absorbance. The aims of this approach are to enhance the specificity and sensitivity of the detection method so that detection can be achieved at low concentrations of analyte or in the presence of high concentrations of interferences.

The pump chosen for delivering the PCR reagent into the mixing chamber is an important factor in this detection method. It has been shown that flow noise resulting from pump pulsations produces most of the baseline noise in a PCR system [180]. For this reason, syringe pumps are often preferred for delivery of the PCR reagent. Alternatively, a simple overpressure pneumatic delivery system may be used.

The mixing apparatus is also crucial to the success of this approach and a variety of different reactors have been suggested. These include a simple tee piece [181], a Y-type device [182], as well as annular membrane [183], packed bed [184, 185] and hollow fibre reactors [185]. The use of an anion-exchange column to both separate

the solute and to act as the post-column reagent generator has also been described [186].

PCR has not been widely applied to the determination of anions in IC, but is often the detection method of choice in the determination of cations, especially for species such as lanthanides and transition metals. Some examples of the use of post-column reactions in anion analysis are the determination of phosphate and polyphosphate [187, 188], NO_2^-, NO_3^-, $S_2O_3^{2-}$, I^- [189] and sulfate [190] via various detection modes.

2.4 SAMPLE CLEAN-UP METHODS

2.4.1 INTRODUCTION

IC is a sophisticated technique which often cannot be applied directly to raw samples since particulate matter can foul the capillary tubing, column, frits and other hardware components. Column efficiency and lifetime also invariably decreases when such samples are used. Excessively high sample pH destroys the equilibria developed between eluent species in the mobile phase and on the column in both suppressed and non-suppressed techniques [14]. This usually results in severe distortion of the analyte peaks as well as the appearance of positive and negative system peaks, especially in a non-suppressed ion chromatographic system. As a result, adequate sample preparation is necessary for the successful separation and subsequent detection of analytes. Sample preparation comprises collection, dissolution and clean-up procedures. With proper sample preparation, a sample free of interfering materials and with a suitable concentration of analyte can be obtained prior to injection onto the ion chromatograph.

Of the above mentioned sample preparation steps, the sample clean-up process, whereby the removal of undesired interferences and particulate matter takes place, is the most important. Samples often contain potential interferences, such as organic material, which must be removed prior to analysis since they can have deleterious effects on the chromatographic column in terms of performance and lifetime, resulting in loss of chromatographic efficiency [191, 192]. Appropriate concentration or dilution of a sample is also sometimes required to obtain good separation and detection of the analyte of interest. Samples having high ionic strength pose detection problems due to the large response and long recovery of conductivity detectors [193]. Analytes occurring in trace levels often require large increments in the enrichment factor so that the detector can give an adequate response. Some of the sample clean-up procedures which can be applied in IC are as follows :

2.4.2 FILTRATION AND SOLID-PHASE EXTRACTION

Generally, filtration is the simplest clean-up process and is used to remove particulate matter from the sample. Filtration is best performed with simple, disposable membrane-based filters of porosity 0.45 μm or less. However, the process is sometimes unreliable for dilute samples due to leaching effects and subsequent sample contamination from the filter. Chloride and nitrate ions are the dominant ions leached from these filters, with fluoride and sulfate leaching to a lesser extent [14]. Ultrafiltration, which is a pressure-driven membrane filtration process, can also be applied for clean-up of difficult samples including the removal of free iodide, calcium and magnesium from biological samples such as serum, milk and egg white [194, 195].

Disposable cartridge columns are used for solid-phase extraction of contaminants from samples. These are available commercially in different packing materials such

as silica, alumina, C_{18} and ion-exchange resins. The clean-up of the sample depends on the column used and also on the inorganic anions of interest. For example, inorganics can be separated from an organic sample matrix by passing the sample through a C_{18} cartridge column [14]. Several practical aspects should receive attention when using cartridge columns, namely column pretreatment, sample flow-rate, method of sample application and sample pH. Common inorganic anions and cations such as F^-, Cl^-, NO_3^-, SO_4^{2-}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} can be leached from a cartridge column and although the concentrations of these ions are very low, sufficient contamination of the sample can occur to render the determination ambiguous.

2.4.3 DIALYSIS

One of the most important approaches to sample clean-up in IC in the use of dialytic methods. Dialysis is a diffusion-based separation process that uses a semipermeable membrane to separate species by virtue of different mobilities through the membrane. The relative rate of transfer of two solutes across a dialysis membrane is a function of both their diffusitivities in the membrane and their driving forces. Separations will be efficient only for species that differ significantly in diffusion coefficient. Dialysis can therefore be defined in terms of a concentration driving force by Fick's first law [196] :

$$J = -D A \frac{dc}{dx}$$

where J, the flux or diffusion rate, is the number of solute molecules that is transported through the membrane per unit time (mol/sec), D is the diffusion coefficient of the solute (m^2/sec), A is the membrane area available for diffusion (m^2) and dc/dx is the concentration gradient across the membrane (mol/m^4). Since diffusion coefficients are a function of molecular size, dialysis is limited in practice to separating species that differ significantly in molecular size. In addition to this

limitation, dialysis is a useful technique only when the solutes to be separated are present in high concentration. This is because solute fluxes in dialysis are directly dependent on the transmembrane concentration gradient. Thus, if the transmembrane concentration gradient is low, practical solute recoveries can be obtained only by increasing membrane area, which may compromise the economics of the process. Because of these considerations, dialysis is characterized by low flux rates in comparison to other membrane separation techniques.

Depending on the membrane used, dialytic techniques can be subdivided into passive dialysis, active dialysis and electrodialysis (when an electrical field is applied to the dialysis process). Passive dialysis is a simple process where diffusion of particles of a specified molecular weight range takes place through a neutral membrane. The process is very slow, in part because it is driven by concentration differences which are usually set by the system. It is not highly selective and often requires a large volume of sample; in addition unacceptable dilution of the sample also may occur. An example of this process is the dialysis of calcium from human serum using a dialysing sample injection system which employs a thin fibre as the dialysis membrane [197]. Since the volume of sample was small (e.g. 40 μl), a very short dialysis time was required.

Active dialysis, which is also called Donnan dialysis (named after Donnan who was the founder of this ubiquitous process), involves the transfer of ions of specified charge through an ion-exchange membrane. For example, if the analyte is an anion, then the process should be carried out with a cation-exchange membrane having negatively charged fixed exchange sites. Ions possessing the *same charge sign* as the exchange sites are referred to as *co-ions* and are excluded from the membrane as a result of electrostatic repulsion. This exclusion is called Donnan exclusion. On the other hand, ions with *opposite charge* to the exchange sites of membrane are called *counter-ions* and are able to permeate the membrane. The choice of

membrane used depends on the analyte of interest. For instance, dialysis of anions requires a cation-exchange membrane, whilst an anion-exchange membrane can be used for cations. Donnan dialysis is a fast, reliable and universal process for sample clean up and enrichment.

A further refinement of the active dialysis method can be achieved by coupling electrical fields with membranes to give a process known as electrodialysis. In electrodialysis, charged species (solute ions) are transferred through the solution and a charged membrane by an electrical driving force. The process is strongly dependent on the electrical potential rather than the concentration potential and usually involves multiple, thin compartments of solutions separated by membranes that allow passage of either cations or anions and block oppositely charged ions. A typical set-up for electrodialysis is shown in Fig. 2.4 which illustrates a desalination process of NaCl solution.

Separation is achieved because charged solutes permeate the membrane to the cathode or the anode, whereas oppositely charged solutes do not and neutral solutes permeate to a much lesser extent. Therefore, selectivity based on charge differences is added to selectivity based on molecular size differences. The molecular flux in electrodialysis can be described by the Nernst-Planck relationship [198]:

$$J = J_{diff} + J_{migr} = -DA\left(\frac{dC}{dx}\right) - \left(\frac{DA\,C\,z\,F}{R\,T}\right)\left(\frac{dV}{dx}\right)$$

where DA is the diffusion coefficient of the analyte, C is the concentration of the analyte (mol/m^3), z is its valency, F is the Faraday constant (C/mol), R is the gas constant (J/mol · K), T is the temperature and dV/dx is the potential difference applied over the membrane (V/m). The first term refers to the diffusional flux J_{diff}, caused by a concentration difference. The second term describes the flux by electrical migration due to a potential difference J_{migr}.

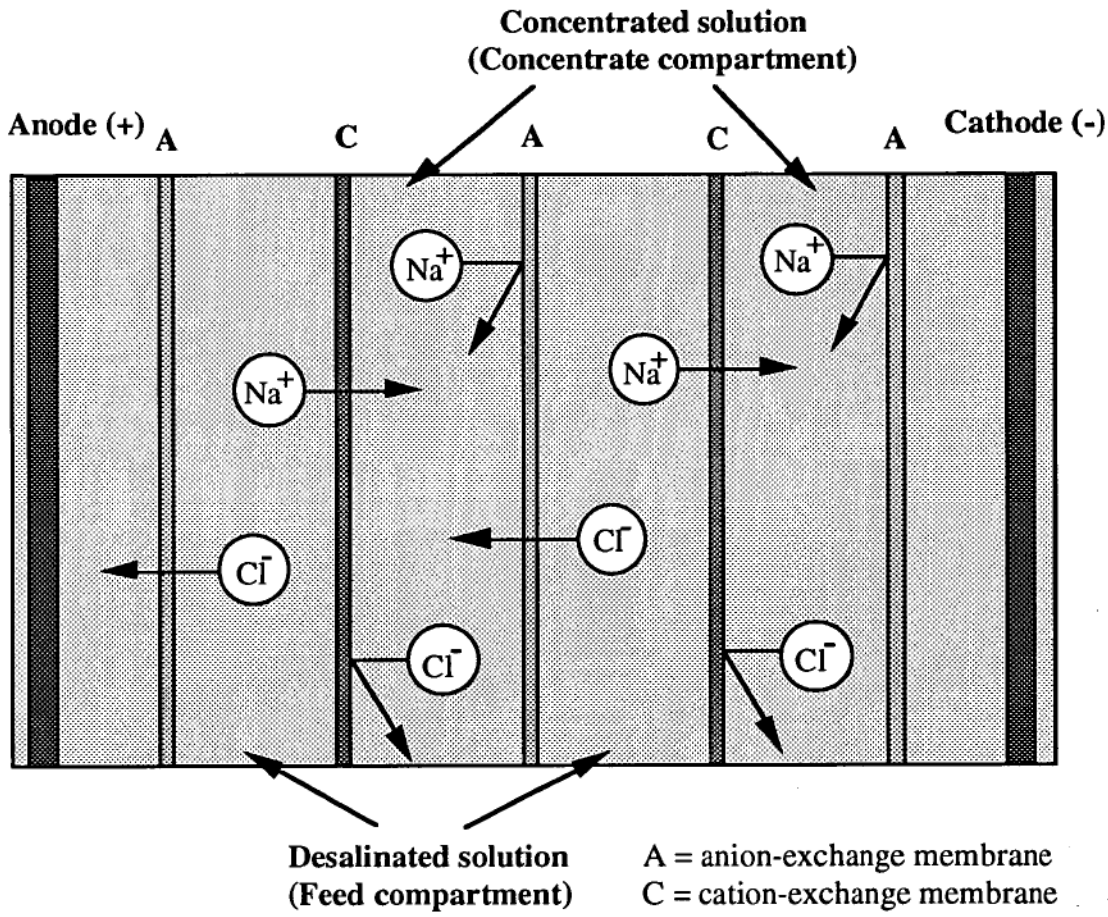


Fig. 2.4 Schematic representation of electrodialysis of NaCl solution.

This equation states that upon applying an electrical field, analyte ions will start to migrate from the feed to the concentrate compartment with their concentration rapidly surpassing the Donnan dialysis equilibrium level. A steady state will be reached when the concentration gradient has increased to such an extent that the diffusion flux equals the migration flux. In practice, further analyte transfer can be effected by increasing the potential difference across the membrane. However this approach is limited by practical problems such as gas bubble formation at the electrodes and a rise in temperature of the solution.

In electrodialysis, both neutral cellulose-based membranes and ion-exchange membranes (as used in Donnan dialysis) are employed. The latter type selectively allows transport of anions while retaining cations or vice versa, according to membrane charge. As the driving force in electrodialysis is fairly strong, ion-exchange membranes do not have to be very thin to obtain a high flux and their thickness typically is about 0.5 mm. The electrodialysis process has a wide range of applications, such as demineralization/deionization of water, concentration of electrolytes, ion replacement reactions, metathesis reactions, separation of electrolysis products and fractionation of electrolytes. Water splitting phenomena or continuous ionization of water is a good example of electrodialysis wherein relatively concentrated solutions of weak acids and bases can be produced from the feed solutions of the corresponding salts. Kassotis and co-workers [199] were able to enrich the concentration of acetic acid up to 19.8% from a feed of 4.8%.

2.4.3.1 Dialytic techniques in ion chromatography

Perhaps the most successful dialytic technique in IC has been active (Donnan) dialysis. Donnan dialysis can be illustrated by reference to the case in which 0.1 M NaCl solution is separated from 0.001 M KCl solution using a cation-exchange membrane [200]. Chemical equilibrium of the counter-ions is reached within a few

hours; however the co-ions attain equilibrium over a long time period as shown in Fig. 2.5. The cations (K^+, Na^+) can diffuse rapidly through the cation-exchange membrane, according to the following equilibrium :

$$Na^+ + K_m^+ \quad \leftrightharpoons \quad Na_m^+ + K^+ \qquad (1)$$

where the subscript m refers to the membrane phase. The equilibrium constant for this exchange is given by

$$K_{Na,K} = \frac{(Na_m^+)\ (K^+)}{(Na^+)\ (K_m^+)} \qquad (2)$$

where the brackets symbolize the activity of the species. Since equilibrium must exist at both surfaces of the membrane, then the expression becomes :

$$\frac{(Na_m^+)_1\ (K^+)_1}{(Na^+)_1\ (K_m^+)_1} = \frac{(Na_m^+)_2\ (K^+)_2}{(Na^+)_2\ (K_m^+)_2} \qquad (3)$$

where the subscripts 1 and 2 refer to the two solutions on either side of the membrane. There can be no concentration gradients for the same ion across the membrane. Therefore,

$$(Na_m^+)_1 = (Na_m^+)_2 \qquad (4)$$

and

$$(K_m^+)_1 = (K_m^+)_2 \qquad (5)$$

Equation (3) can be simplified to give equations (6) or (7) if the activity coefficient is assumed to be unity

$$\frac{(Na^+)_1}{(Na^+)_2} = \frac{(K^+)_1}{(K^+)_2} \qquad (6)$$

and

$$\frac{[Na^+]_1}{[Na^+]_2} = \frac{[K^+]_1}{[K^+]_2} \qquad (7)$$

where the brackets represent molar concentrations.

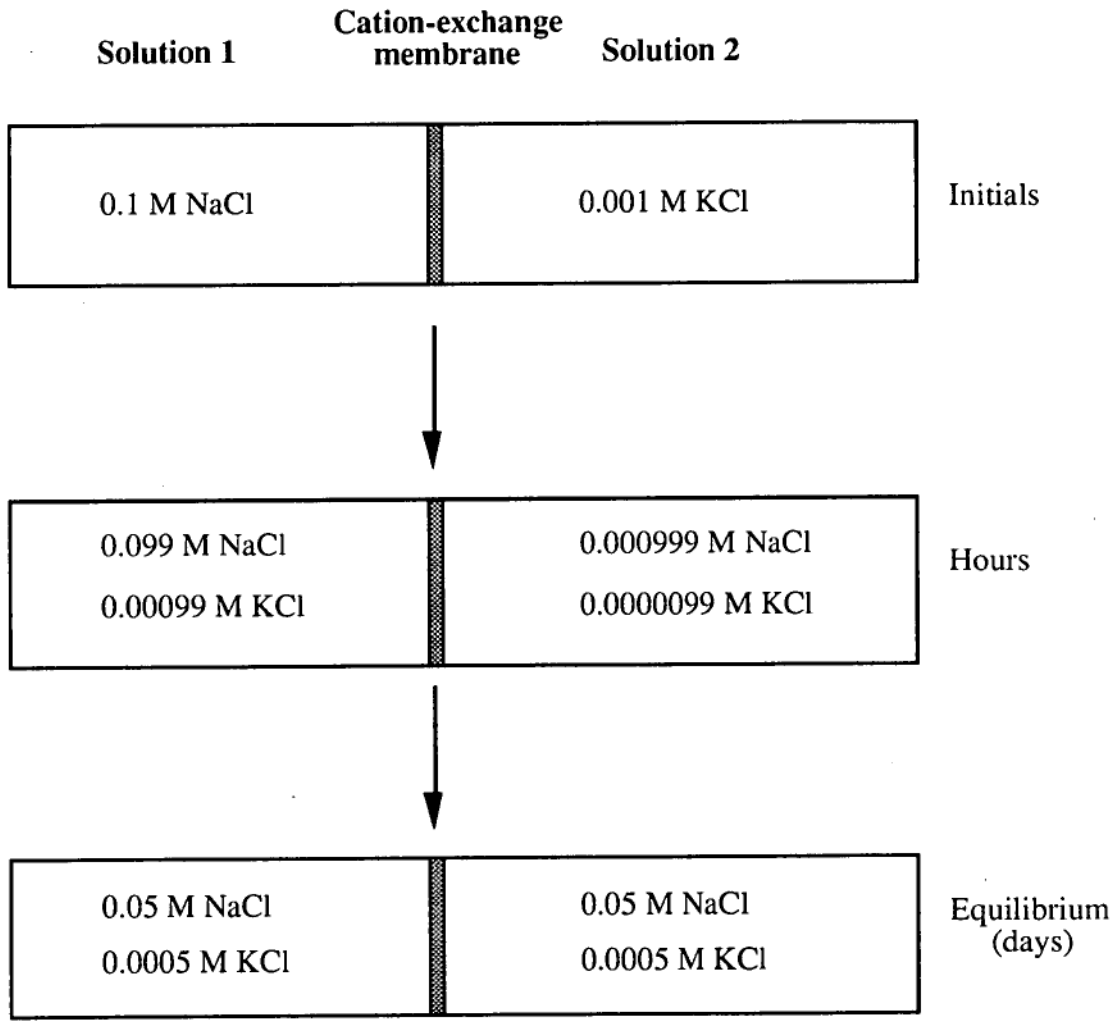


Fig. 2.5 Donnan dialysis of KCl and NaCl.

Sodium ions tend to diffuse from the region of high concentration (solution 1) to the region of low concentration (solution 2). The diffusion of potassium ions maintains the electroneutrality of the system. Thus, 99% of potassium has diffused from solution 2 to 1 (i.e. from low concentration to high) accompanied by 1% diffusion of sodium ion from solution 1 to 2. The process, at the end, attains Donnan equilibrium. This also illustrates the concomitant sample preconcentration that occurs [14].

The potential achieved in this process is called the Donnan potential or membrane potential, caused by an unequal distribution of free ions due to the dialysis which eventually results in an osmotic pressure and an electrical difference between the two solutions. The chemical equilibrium described here is a Donnan equilibrium. There are three important factors which are solely responsible for the Donnan equilibrium i.e. unequal distribution of charged ions, osmotic pressure and the potential differences between the two phases.

Donnan dialysis is a good method for matrix normalization for certain cation samples, such as Cu^{2+}, Pb^{2+} and Cd^{2+}, as part of the process of ion chromatographic sample clean-up [201]. A ten minute dialysis is adequate to eliminate the matrix effects of surfactants, complexing reagents and electroactive compounds. Donnan dialysis has also been used for preconcentration of both anions and cations. It is relatively simple, inexpensive and precise for the preconcentration of trace ions from samples of both high and low ionic strength. Up to an 80 fold increase in concentration can be obtained for a one hour dialysis when a receiver electrolyte having a higher ionic strength than the sample is used [193]. The enrichment factor achieved with Donnan dialysis also depends on the rate of ion transport through the membrane. Membrane structure, sample volume, dialysis time, sample flow-rate and receiver solution composition also play a vital role in the preconcentration of

analytes. Use of a conditioned tubular membrane with a recirculating receiver solution has been shown to give optimal enrichment factors [202-206].

A minimum of interaction between the fixed site of the membrane and the test ion maximizes the transport rate in Donnan dialysis. It has been noted that Donnan dialysis of cations into a $NaNO_3$ receiver electrolyte is suppressed by interaction between the fixed sulfonate exchange-site on the cation-exchange membrane and the test cations [207]. Blaedel and Kiesel [208] found that the initial transfer rate of the species into a small volume (about 0.01 ml) of concentrated receiver electrolyte was proportional to the concentration of the ion of interest in the sample. The rate of Donnan dialysis, which determines the enrichment factor, is often independent of sample pH. The highest enrichment factors (i.e. the concentration of the analyte in the diluted receiver after dialysis divided by initial concentration) are usually obtained by use of a low flow-rate of the receiver electrolyte due to the longer residence time on the ion-exchange membrane. However, greater efficiency is found at higher flow-rates when the enrichment factor is expressed per unit time [209].

Donnan dialysis has a wide range of applications in the separation and speciation of metal ions in cases where receiver electrolyte composition can be used to influence the chemistry at the sample membrane interface during dialysis. The process can provide the basis for a rapid estimation of the total soluble metal (including free metal ion plus labile complexed and non-labile complexed metal) [210]. Dialysis has also been shown to be a promising technique in the clean-up of samples in a plating bath, such as metal cyano-complexes, using an anion exchange membrane; chloride, nitrate and sulfate in concentrated NaOH using a cation-exchange membrane; sulfate in NaCl using an anion-exchange membrane; and chloride in polyelectrolytes (e.g. polyacrylic acid) using an anion-exchange membrane.

Electrodialysis has been used for many years in industry for water purification, waste water treatment and desalination procedures [211-214]. On the analytical scale, the method has been reported for the treatment of strongly acidic samples prior to the determination by IC of magnesium (II) and calcium (II), using a dual anion-exchange membrane tube device [215]. Electrodialytic clean-up of biological samples [216] and on-line electrodialytic treatment for HPLC determination of environmental samples [217, 218] have also been described but no study has been reported on the use of this technique for the determination of inorganic anions by IC.

2.4.3.2 Membranes used for dialysis

2.4.3.2.1 Introduction

The French scientist Abbe Nollet was the first to study "membrane phenomena" in 1748 and demonstrated the semipermeable character of membranes. In 1855, Fick coined the word "diffusion" through a membrane. In the middle of the nineteenth century, Thomas Graham cited the term "dialysis" using synthetic membranes. Almost at the same time, Traube, Pfeffer and van't Hoff were studying osmotic phenomena through membranes. In 1911, Donnan developed the new phenomenon of dialysis using a membrane. The process is referred to as Donnan dialysis. He was also responsible for the Donnan distribution law using semipermeable membranes.

Membranes are now applied extensively to a variety of separations, such as particulates from solution, salts from water, toxins from blood and one gaseous component from a gas mixture. A number of membrane separations and membrane application processes are shown in Fig. 2.6 [219]. The membrane has a key role in the process of dialysis. The extent of separation depends upon a number of characteristic properties such as nature, structure, composition and configuration, since the membrane is the major determinant for separation of analytes.

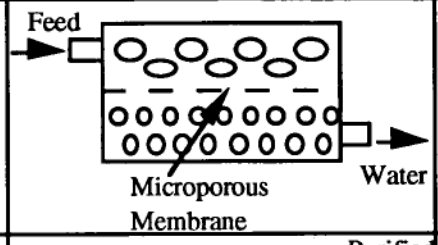
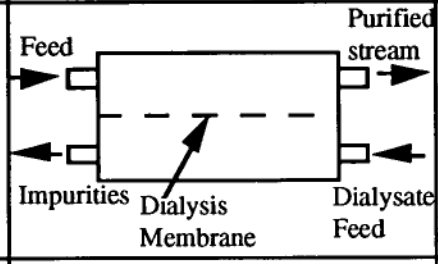
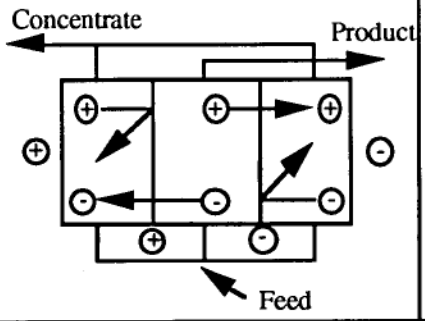
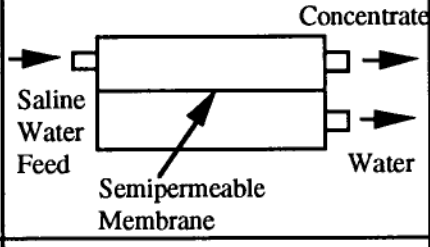
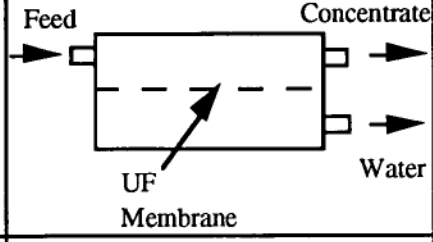
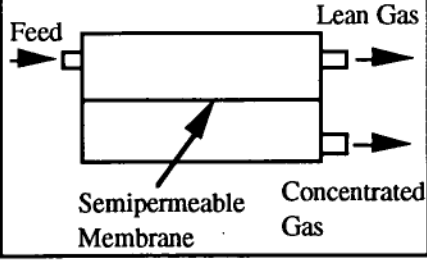
PROCESS	CONCEPT	MATERIALS PASSED	DRIVING FORCE	MATERIAL RETAINED
Micro-filtration		Water and Dissolved Species	Pressure Difference, Typically 10 psi	Suspended Material (Silica, Bacteria, etc.) Variable Particle-Size Cutoffs
Dialysis		Ions and Low Molecular-Weight Organics (Urea, etc.)	Concen-tration Difference	Dissolved and Suspended Material with Molecular Weight > 1,000
Electro-dialysis		Ions	Voltage, Typically 1-2 V/Cell Pair	All Non-Ionic and Macromolecular Species
Reverse Osmosis		Water	Presure Difference, Typically 100-800 psi	Virtually All Suspended and Dissolved Material
Ultra-filtration		Water and Salts	Pressure Difference, Typically 10-100 psi	Biologicals, Colloids and Macromolecules. Variable Molecular-Weight Cutoffs
Gas Separation		Gases and Vapors	Pressure Difference, Typically 1-100 atm	Membrane-Impermeable Gases and Vapors

Fig. 2.6 Membrane separation and application processes [219].

2.4.3.2.2 Structure and properties of membranes

In a general sense, a membrane is an interphase separating two phases of different concentrations. The membrane phase acts as a barrier to the flow of molecular or ionic species present in the solution. More specifically, it restricts the transport of various chemical species in a rather specific manner [220].

A membrane can be homogeneous or heterogeneous, and symmetrical or asymmetrical in its structure. It may be neutral or may carry some specific charges, either positive or negative, or it may have both. The thickness of the membrane varies from 100 nm to more than a centimeter. Helmcke classified the membrane according to pore size as very fine, fine, medium and coarse-porous. Pore sizes vary according to the structure of membrane [221].

The important physical properties of the membrane are selectivity, transport capacity and permeability. The flow of species through the membrane depends on the transport number of the membrane. High selectivity gives good separation from the mixture of samples. Permeability depends on the pore size of the membrane. Therefore, the rejection of micro or macromolecules depends upon permeability of the membrane.

For membrane separation processes, only the driving forces which can lead to a significant flux of matter are of practical importance. These driving forces are hydrostatic pressure, concentration and electrical potential differences. Hydrostatic pressure difference between two phases separated by a membrane occurs when the hydrodynamic permeability of the membrane is different for different components. Concentration difference is caused by the different diffusity and concentration of various chemical species in the membrane, and different mobility of charged particles in the membrane causes a difference in the electrical potential [220]. It has

to be pointed out, however, that the overall driving force for the transport of a chemical species through a membrane is the gradient in its chemical potential, which consists of additional terms to the three factors above. The most important part in a membrane separation process is obviously the membrane itself. Membranes may vary significantly in their structure and in the way they function, depending on the area of application.

2.4.3.2.3 Ion-exchange membranes

In the process of Donnan dialysis, a concentration gradient is the driving force and ion-exchange membranes play a key role. This is due to their characteristic property of having a high value for the transport number. These membranes have proved to be very useful in sample clean-up procedures and are also of industrial importance. Regarding their fixed inorganic groups present as a fixed exchange site, there are two kinds of ion-exchange membrane, namely cation-exchange and anion-exchange membranes.

In the case of cation-exchange membranes, negative functional groups such as $-SO_3^-$, $-COO^-$ are present, whilst positive functional groups such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$ (where R is an alkyl group) are present in the case of anion-exchange membranes. The membranes exclude the co-ions with respect to the fixed exchange-site by electrostatic repulsion and the amount of exclusion depends on the concentration of the external electrolyte with which the membranes are in equilibrium.

The separation of analytes using a membrane is essentially due to the different molecular interactions between permeant molecules and the membrane *via* adsorption, diffusion and desorption. The different selectivity of solutes in a solution for a given membrane can, therefore, be characterized by molecular size, shape and the intermolecular interaction potential. Loeb and Sourirajan [222] found

the order of selectivity for anions was - citrate > tartarate = sulfate > acetate > chloride > bromide > nitrate > iodide > thiocyanate and for cations - magnesium, barium, strontium, calcium > lithium, sodium, potassium on the basis of electromotive potential, the unhydrated ionic radius, the ionic charge and the dielectric constant.

The capability of an ion-exchange membrane to exclude co-ions is defined by the term permselectivity of the membrane which is the difference in diffusibility between ions of opposite charge. Excluded co-ions occur in a relatively low concentration in the membrane phase compared to the exchangeable counter-ions [223]. Permselectivity may decrease with an increase in concentration of the electrolyte in the solution surrounding the membrane [224].

Sometimes the permselectivity of a membrane tends to fail and its ability to perform a certain sample dialysis is lost. For instance, Donnan dialysis of sodium hydroxide into a sulfuric acid receiver by a cation-exchange membrane shows a leakage of sulfate ion (co-ion). This leaking of sulfate ion is due to the low charge density of the membrane caused by excessive swelling with water. Also, the high ionic strength of the electrolyte causes partial breakdown of the membrane's permselectivity. The incursion of the conjugate base of the acid is due to the high ionic strength of the solution wherein both sides of the membrane come in contact and, therefore, breakdown of the Donnan exclusion theory occurs. This practical failure of Donnan dialysis is overcome by the introduction of "dual ion-exchange" phenomenon. Cox and Tanaka have performed the dialysis using a slurry of ion-exchange resin in the hydrogen form as a receiver instead of sulfuric acid [225]. Since the counter-ion in the receiver solution is the resin bead itself, it is physically (as well as electrostatically) precluded from entering the sample. Polarity and pore size of the resin are the most important characteristics for the exchange capacity [226].

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CHAPTER THREE

EXPERIMENTAL

3.1 INTRODUCTION

The aim of this chapter is to describe the instrumentation, the basic arrangement used for the ion chromatograph, together with the reagents and samples that were used in the course of this work. Further specific details are also given in the experimental sections for each following chapter in this thesis.

3.2 INSTRUMENTATION AND APPARATUS

Table 3.1 lists the ion chromatographic instrumentation, which was operated on both suppressed and non-suppressed modes, and the ion-exchange columns which were utilized throughout this study. The basic chromatographic instrumentation for both separation modes was the same, except for the use of a suppressor and regenerant pump in the suppressed mode, as shown schematically in Fig. 3.1. Other miscellaneous equipment employed in this study is listed in Table 3.2.

TABLE 3.1

LIST OF CHROMATOGRAPHIC EQUIPMENT USED

Apparatus	Model	Supplier
Injector	U6K	Millipore-Waters, Milford, MA, USA

TABLE 3.1 cont...

Apparatus	Model	Supplier
Single piston pump	M 45	Millipore-Waters, Milford, MA, USA
Dual piston pump	M 510	Millipore-Waters, Milford, MA, USA
Conductivity detector	M 430	Millipore-Waters, Milford, MA, USA
Cation-exchange column	Waters IC Pak C	Millipore-Waters, Milford, MA, USA
Anion-exchange columns	Waters IC Pak A and Waters IC Pak A HR	Millipore-Waters, Milford, MA, USA
Anion-exchange column	Dionex HPIC AS-4A	Dionex Co., Sunnyvale, CA, USA
Guard column	Dionex AG-4A	Dionex Co., Sunnyvale, CA, USA
Suppressor	Dionex AMMS	Dionex Co., Sunnyvale, CA, USA
Strip-chart recorder	Cole-Parmer L-08373-10	Cole-Pamer, Chicago, Illinois, USA
Chromatography workstation	Maxima 820 data station	Millipore-Waters, Milford, MA, USA
Regenerant pump device	Reagent Delivery Module (RDM)	Millipore-Waters, Milford, MA, USA
Switching valve	Six-port switching valve fitted with 20 µl injection loop	Millipore-Waters, Milford, MA, USA

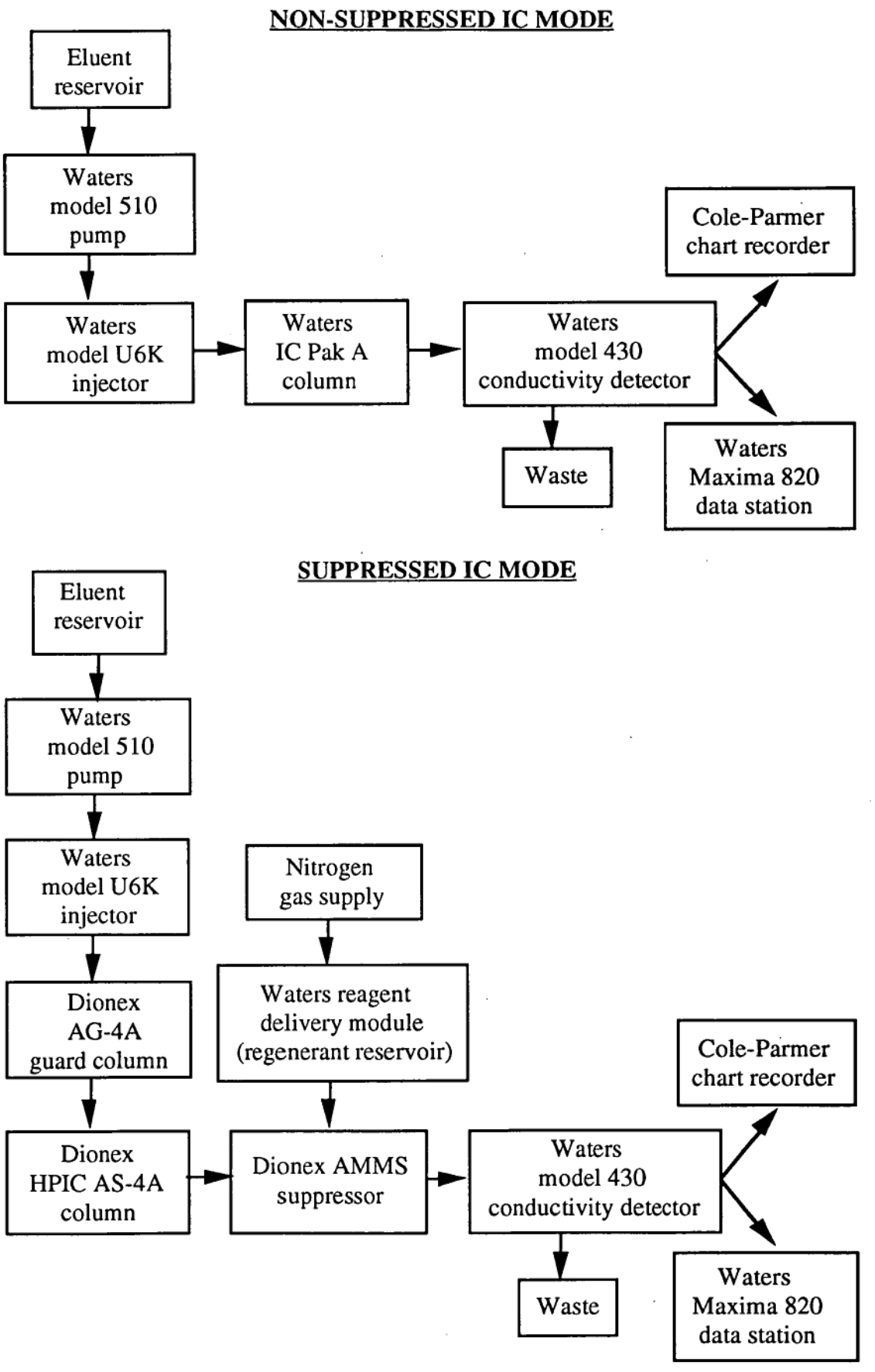

Fig. 3.1 Schematic diagram of ion chromatographic modes employed in this study.

TABLE 3.2

LIST OF MISCELLANEOUS EQUIPMENT USED IN THIS STUDY.

Apparatus	Model	Supplier
Capillary Electrophoresis	Quanta 4000	Millipore-Waters, Milford, MA, USA
pH electrode	BJ-312	Activon, Sydney, Australia
pH meter	101	Activon, Sydney, Australia
HPLC water purification system	Milli-Q water purification system	Millipore, Bedford, MA, USA
HPLC water filtration system	n.a.	Millipore-Waters, Milford, MA, USA
Ultrasonic bath	FX-12	Unisonics, Sydney, Australia
DC power supply	GPR-7530D	GoodWill, Taiwan
Electrophoresis power supply	3000 Xi	BioRad, Richmond, CA, USA
Syringe pump	A-99	Razel Sci. Inst., Inc., Stamford, CT, USA
Muffle furnace	GLM 11/3	Carbolite, Bamford, Sheffield, England
pH indicator sticks	pH range 1 - 14	Merck & Co., Inc., Rahway, NJ, USA
Glass syringes	50 µl, 100 µl, 500 µl	Scientific Glass Engineering, Vic., Australia

n.a. : not applicable

3.3 REAGENTS AND PROCEDURES

HPLC grade water was used for preparing both the mobile phases and analyte solutions and was purified by passing doubly distilled water through a Millipore (Bedford, MA, USA) water purification system, then filtered through a 0.45 μm type HA filter.

3.3.1 ELUENT PREPARATION

Stock solutions of the eluents were prepared by dissolving the required amounts of the appropriate solid or liquid chemicals in approximately 800 ml of Milli-Q water in 1 L volumetric flasks which were then made up to 1 L with Milli-Q water after adjusting the pH (wherever necessary) by dropwise addition of an appropriate acid or base. The pH of the eluents was measured using an Activon (Sydney, Australia) model 101 mV/pH meter with a glass electrode. The eluents were prepared daily by diluting the stock solutions with Milli-Q water and were degassed in an ultrasonic bath prior to use. Details of actual eluents are given in the appropriate experimental sections or as captions to the figures.

3.3.2 STANDARD SOLUTIONS

The stock standard solutions were prepared by weighing appropriate amounts or pipeting appropriate volumes to give :

(i) 1,000 μg/ml of common inorganic anions (present as sodium salts).

(ii) 1 M solutions of sulfuric acid and sulfonic acids, with the exception of octanesulfonic acid which was prepared by passing a solution of 1 M sodium octanesulfonate through a glass column packed with 100 g BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200-400 mesh.

Working solutions of mixtures of inorganic anions were prepared by diluting the

stock solutions with Milli-Q-water and with sodium hydroxide to give final concentrations of 0.1-1.0 M NaOH. Both the stock and working solutions of (i) and (ii) were prepared in glass volumetric flasks and stored in polypropylene containers.

3.3.3 REAGENTS

Table 3.3 lists the reagents used in the preparation of mobile phases and standard solutions in this study, along with the relevant grade and supplier details.

TABLE 3.3
LIST OF REAGENTS, GRADE AND SUPPLIER DETAILS FOR THE PREPARATION OF STANDARD SOLUTES AND MOBILE PHASES

Chemical	Grade	Supplier
Standard solutions		
Sodium bromide	AR	Ajax, Sydney, Australia
Sodium chloride	AR	Ajax, Sydney, Australia
Sodium fluoride	AR	BDH, Vic., Australia
Sodium nitrate	AR	Ajax, Sydney, Australia
Sodium nitrite	AR	Ajax, Sydney, Australia
Sodium phosphate	AR	Ajax, Sydney, Australia
Sodium sulfate	AR	Ajax, Sydney, Australia
Mobile phases		
Acetonitrile	Spectrograde	Ajax, Sydney, Australia
Boric acid	AR	Ajax, Sydney, Australia

TABLE 3.3 cont...

Chemical	Grade	Supplier
Di-sodium EDTA	AR	Ajax, Sydney, Australia
Glycerol	AR	BDH, Poole, England
D-tartaric acid	AR	Ajax, Sydney, Australia
Nitric acid	AR	M&B, Australia
Sodium bicarbonate	AR	Ajax, Sydney, Australia
Sodium carbonate	AR	Ajax, Sydney, Australia
Sodium D-gluconate	AR	Fluka, Switzerland
Sodium tetraborate decahydrate	AR	M&B, Australia
Hydrogen ion donating media		
1-Camphorsulfonic acid	AR	Sigma, St. Louis, USA
1-Octanesulfonic acid (Na-salt)	AR	Sigma, St. Louis, USA
Methanesulfonic acid	LR	Tokyo Kasei, Tokyo, Japan
p-Toluenesulfonic acid	AR	Sigma, St. Louis, USA
Solid-phase reagent (SPR)	450 meq/l	Millipore-Waters, Milford, MA, USA
Sulfuric acid	AR	Ajax, Sydney, Australia
BioRad AG 50W-X8 cation-exchange resin	hydrogen form, 200-400 mesh	BioRad Laboratories, Richmond, CA, USA
BioRad AG 50W-X2 cation-exchange resin	hydrogen form, 200-400 mesh	BioRad Laboratories, Richmond, CA, USA

TABLE 3.3 cont...

Chemical	Grade	Supplier
Amberlite IRC-50 cation-exchange resin	hydrogen form, 50-100 mesh	Sigma, St. Louis, USA
Amberlite IR-120 cation-exchange resin	hydrogen form, 50-100 mesh	Sigma, St. Louis, USA
General chemicals		
Hydrochloric acid	AR	Ajax, Sydney, Australia
Sodium hydroxide	AR	Ajax, Sydney, Australia
Potassium sulfate	AR	Ajax, Sydney, Australia
Potassium chloride	AR	Ajax, Sydney, Australia
Nitrogen gas	Industrial	Ajax, Sydney, Australia

Abbreviations:

LR : Laboratory grade reagent

AR : Analytical grade reagent

BDH : British Drug Houses

M&B : May And Baker

3.3.4 CHROMATOGRAPHIC PROCEDURES

The ion chromatographic measurements were carried out at room temperature. The chromatograms were recorded on a Cole-Parmer (Chicago, Illinois, USA) strip-chart recorder or on a Millipore-Waters (Milford, MA, USA) Maxima 820 data station which was used for automatic measurement of analyte peaks [1]. The speed of the chart recorder was 0.5 cm/min and the mobile phase flow-rate was 1.2 ml/min. A Waters Reagent Delivery Module (RDM), which is designed to provide pulse-free

reagent delivery [2], was used to pass the regenerant through the AMMS suppressor in the suppressed IC mode. The regenerant used for suppressing the conductivity of the eluent was 25 mN H_2SO_4 and the regenerant flow-rate was 1.5 ml/min as suggested by the manufacturer [3]. Further details of the chromatographic procedures are given in the experimental sections in each chapter or as captions to figures.

3.4 REFERENCES

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CHAPTER FOUR

DONNAN-DIALYTIC CLEAN-UP OF ALKALINE SAMPLES PRIOR TO ION CHROMATOGRAPHIC ANALYSIS

4.1 INTRODUCTION

Samples of extreme pH (i.e. outside the pH range 3-11) often pose problems in ion chromatographic determinations because of deleterious effects on the column life and performance [1]. In particular, strongly alkaline samples may give distorted analyte peaks, system peaks and severe baseline perturbations due to the effect of the injected sample on the acid-base equilibria existing in the eluent in both suppressed and non-suppressed IC. Whilst these problems can sometimes be circumvented through the use of selective detectors or specially designed eluents, adequate sample clean-up steps are generally required to ensure the ultimate success of the analysis.

Sample clean-up may involve the removal of undesired particulate matter, the reduction in concentration or complete removal of potential interferences, or concentration of the analyte of interest to improve detection. Samples of high ionic strength are often troublesome due to the large response and long recovery of the conductivity detectors. When the high ionic strength of the sample is due to the presence of elevated levels of sodium hydroxide, simple neutralization of the sample is unsuitable because the resultant high level of the acid anion would also be likely to cause interference problems. However, two alternative methods of sample clean-up are applicable.

The first involves treatment of the sample with a cation-exchange resin in the

hydrogen form, which results in replacement of sodium in the sample with hydrogen ions from the resin, leading to neutralization of the sample. This treatment can be accomplished using a batch method by which the ion-exchange resin is added to the sample, or using a column method by which the sample is passed through a small column packed with suitable resin [2]. The second approach to sample clean-up uses an active or Donnan dialysis treatment with a suitable membrane. In this case, the membrane is usually functionalized with sulfonic acid groups to impart cation-exchange characteristics; dialysis occurs between the sample solution on one side of the membrane and an acidic solution on the other side. Again, exchange of sodium ions for hydrogen ions leads to sample neutralization and the mechanism of operation is identical to that used in membrane-based suppressors employed in suppressed IC. The physical form of the membrane may vary, with flat sheets [3] or hollow fibres [4] being used.

The Donnan dialysis process involves the transfer (diffusion) of ions of positive charge through the cation-exchange membrane. The process is based on the theory of ion-exchange phenomena through an ion-exchange membrane. The diffusion of ions through the membrane results from unequal distribution of ions, osmotic pressure and potential differences between the phases surrounding the membrane. The efficiency of diffusion depends on the ion-exchange capacity of the membrane. The selective permeability of the ion-exchange membrane towards ions of a specific charge is the most important characteristic property of the membrane. The exchange rate of ions also depends on the porosity, thickness and fixed charge density of the membrane. Apart from ion-exchange capacity, the membrane should fulfill the following requirements [5] :

1. High permselectivity and low electrical resistance.
2. High mechanical, chemical and thermal stability.
3. A fairly low swelling or shrinking behaviour with charge of the surrounding electrolyte concentration.

Theoretically, when a sample solution is passed through a cation-exchange membrane which possesses a negative inorganic group as the fixed exchange site, exchange of the counter-ions (with respect to the fixed exchange site) takes place between sample and the medium electrolyte. Anions possess the same charge sign as the exchange site and, in theory, are excluded from diffusion through the membrane by electrostatic repulsion that occurs between the two negative ions. The extent of exclusion (expressed as the permselectivity of the membrane) depends on the concentration of the external electrolyte with which the membrane is in equilibrium, and decreases as this concentration is increased [6]. The Donnan dialysis process is illustrated in Fig. 4.1. In the diagram, sulfuric acid is the surrounding medium. A sample solution of sodium hydroxide having a high pH is passed through the membrane, where exchange of Na^+ and H^+ occurs, but the OH^- ions are retained within the membrane tubing by repulsion from the membrane exchange sites and are later collected as the dialysate.

Due to the incursion of H^+ into the sample compartment to form H_2O, the NaOH is neutralized and the pH of the sample is lowered. In certain instances, incursion of sulfate ion in the diagram above may occur, especially when a high concentration of sulfuric acid is used, thereby exerting high osmotic pressure causing diffusion of the sulfate ions through the membrane. Permselectivity of the membrane may also decrease when the membrane shows excessive swelling in water, due to the resultant low charge density of functional groups on the membrane. Thus, the concentration of the acidic medium used as a source of hydrogen ions for the dialysis process is limited by the permselectivity of the membrane towards the anion of the acid employed.

One method which may be used to overcome this problem is described as "dual ion-exchange" dialysis [7]. Here, an aqueous slurry of cation-exchange resin in the hydrogen form is used as the source of hydrogen ions instead of an acidic solution.

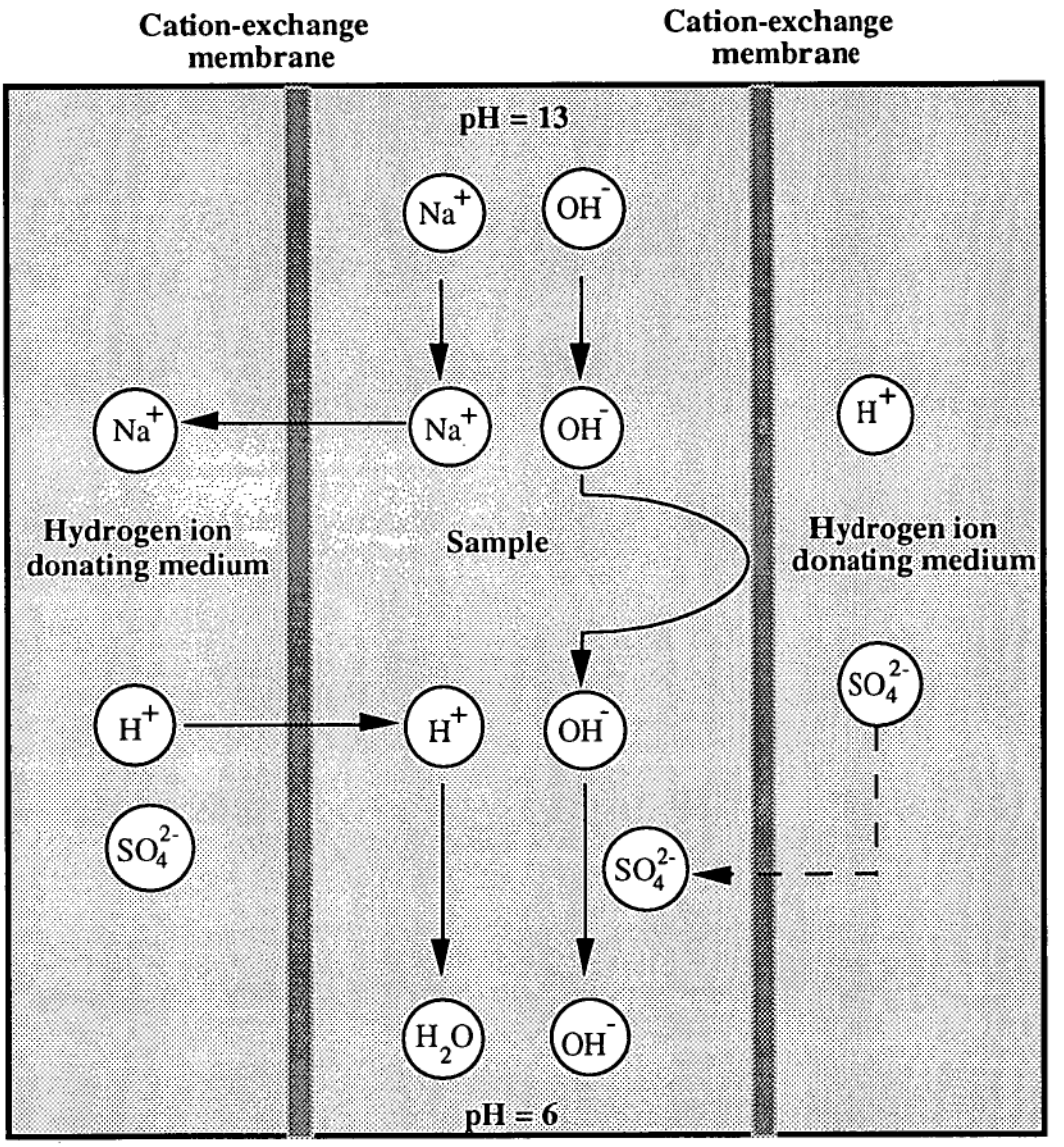


Fig. 4.1 Theoretical diagram of Donnan dialysis.

The acid anion is now a resin bead and its incursion through the membrane is physically precluded. Moreover, the change in concentration of an analyte ion in the sample solution either through contamination effects, adsorption losses or sample volume change which commonly feature in conventional ion-exchange is also minimized.

In this work Donnan dialysis procedure was used for pretreatment of alkaline solutions prior to ion chromatographic analysis. It was carried out by passing sodium hydroxide solutions containing common inorganic anions through a cation-exchange hollow fibre which was immersed in a hydrogen ion donating medium. Dialysis devices were constructed for this purpose with the use of various cation-exchange hollow fibres. The efficiency and neutralization capacity of these devices with a range of hydrogen ion donating media (including cation-exchange resins) were evaluated.

4.2 EXPERIMENTAL

4.2.1 INSTRUMENTATION

The ion chromatograph consisted of a Millipore-Waters (Milford, MA, USA) model 510 pump, model U6K injector and model 430 conductivity detector. The column used was a Millipore Waters IC Pak A anion column, 50 x 4.6 mm ID, packed with polymethacrylate anion-exchange resin with quaternary ammonium functionalities.

The chromatography was carried out at room temperature. The chromatograms were recorded on a Cole-Parmer (Chicago, Illinois, USA) chart recorder and on a Millipore-Waters 820 Maxima Data station. The chart speed of the recorder was 0.5 cm/min and the mobile phase flow-rate was 1.2 ml/min throughout the experiment.

50 µl aliquots of dialysate was chromatographed using a 100 µl glass syringe (Scientific Glass Engineering, Vic., Australia).

4.2.2 DIALYSIS DEVICES

Two sample treatment dialysis devices were constructed for the dialysis process and three types of cation-exchange hollow fibres were employed during the experiment. The first dialysis device for the comparison of hydrogen ion donating media utilized a cation-exchange hollow fibre which was made of polystyrenedivinylbenzene with fixed site sulfonic groups as the ion-exchanger. The hollow fibre was protected by a woven polymer sheath and both ends had a syringe connector held fast by a piece of heat shrink tubing. The fibre (30 cm x 1.2 mm ID) was immersed in a solution of hydrogen ion donating medium placed in a glass tube (10 cm x 24 mm ID). A plastic syringe was used to pass the sample through the fibre and a 10 cm length of teflon tubing was fitted to the other end allowing passage of the sample out from the fibre. The dialysate sample was collected in a small sample tube for analysis by IC. The system was assembled as shown in Fig. 4.2.

The second dialysis device employed a 160 cm x 0.6 mm ID Du Pont (Delaware, USA) Nafion cation-exchange hollow fibre packed with polystyrenedivinylbenzene beads (packed fibre), coiled on a holder made of glass rods and placed in a housing tube made from clear acrylic material (20 cm x 25 mm ID) containing a solution of hydrogen ion donating medium. A 345 cm x 0.5 mm ID Du Pont Nafion cation-exchange hollow fibre (unpacked fibre), assembled in the same way as the packed fibre was also used. A Millipore-Waters M45 pump was used to pass the sample through the hollow fibre and the effluent was collected in a small sample tube. The arrangement of the device is shown in Fig. 4.3. This device with the two types of cation-exchange hollow fibres was used for comparison of fibre types and the study of the neutralization capacity of the device.

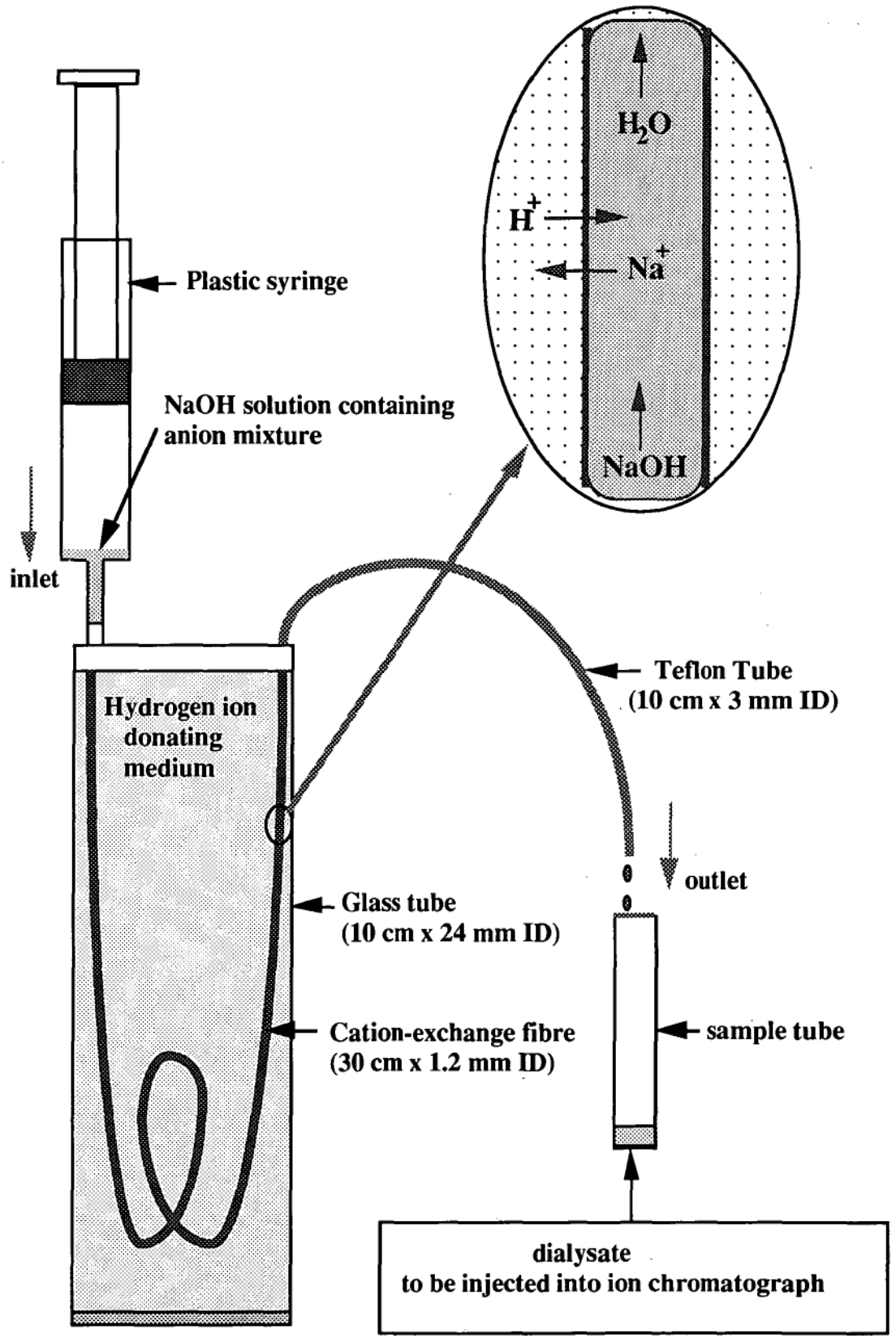


Fig. 4.2 Sample clean-up device used for the comparison of H^+ donating media.

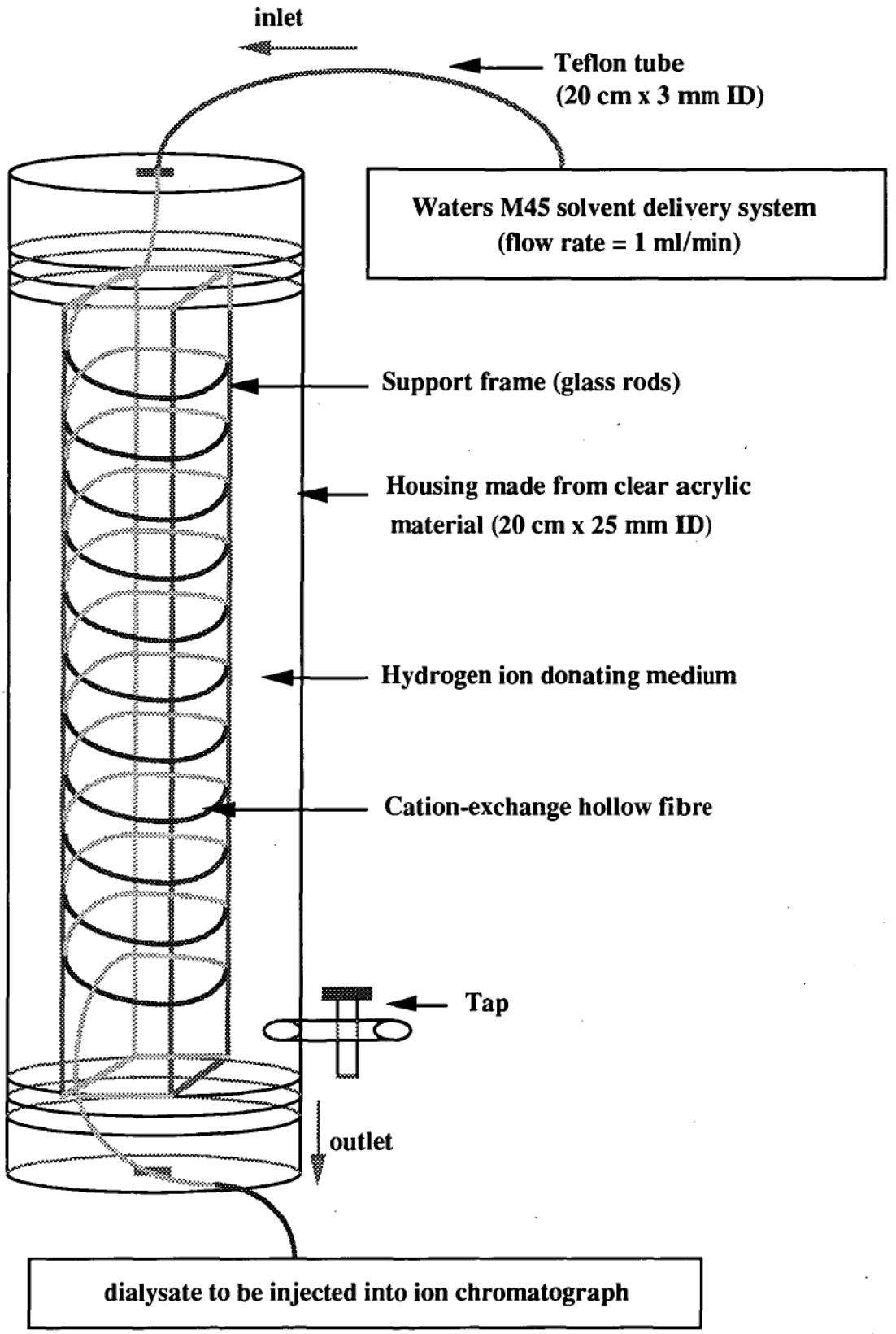


Fig. 4.3 Sample clean-up device used for the comparison of fibre types and the neutralization capacity of dialysis device.

4.2.3 REAGENTS

All chemicals used were of analytical reagent grade and the water used in the preparation of standard solutions and eluents was purified on a Millipore (Bedford, MA, USA) Milli-Q water treatment system. All samples and mobile phase solutions were filtered through a Millipore type HA 0.45 μm membrane filter and degassed in an ultrasonic bath prior to use.

A stock solution of mobile phase for ion chromatographic separation was prepared by dissolving 16 g of sodium gluconate, 18 g of boric acid and 25 g of sodium tetraborate in 1L of Milli-Q water. The mobile phase was prepared by mixing 20 ml of this stock solution with 2.5 ml of glycerol and 120 ml of acetonitrile, after which the pH was adjusted to 8.5 by dropwise addition of a sodium hydroxide solution and diluted to 1L with Milli-Q water.

4.2.3.1 Standard solutions

Standard stock solutions of anions were prepared by dissolving sodium salts in degassed and filtered Milli-Q water. Mixtures of 5-6 anions in various concentrations of sodium hydroxide solutions were then prepared from stock solutions and are listed in Table 4.1.

4.2.3.2 Hydrogen ion donating media

Comparison of hydrogen ion donating media

The hydrogen ion donating solutions compared initially were sulfuric acid (H_2SO_4), methanesulfonic acid (MSA), octanesulfonic acid (OSA), camphorsulfonic acid (CSA) and p-toluenesulfonic acid (TSA). All were prepared to concentrations of 0.1 M, 0.3 M. 0.5 M, 0.7 M and 1.0 M, with the exception of octanesulfonic acid which

was prepared by passing a solution of 1.0 M sodium octanesulfonate through a glass column packed with 100 g of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200-400 mesh.

Dual ion-exchange processes were performed with slurries of cation-exchange resins as listed below :

1. BioRad AG 50W-X8, 200-400 mesh, hydrogen form (AG 50W-X8).
2. BioRad AG 50W-X2, 200-400 mesh, hydrogen form (AG 50W-X2).
3. Amberlite IRC-50, 50-100 mesh, hydrogen form (IRC-50).
4. Amberlite IR-120, 50-100 mesh, hydrogen form (IR-120).

The cation-exchange resin was soaked in Milli-Q water for several hours, filtered on a Buchner funnel and rinsed thoroughly with Milli-Q water prior to use. A slurry of the resin was prepared by adding 25 g of resin with 10 ml of Milli-Q water.

TABLE 4.1
LIST OF INORGANIC ANIONS USED IN THIS STUDY.

Stage of Experiment	Anions (µg/ml) in NaOH solutions of concentration 10^{-4} M, 10^{-3} M, 10^{-2} M and 10^{-1} M
Comparison of hydrogen ion donating media	F^-(30), Cl^-(50), NO_2^-(100), Br^-(100), NO_3^-(100), SO_4^{2-}(100)
Comparison of fibre types	F^-(30), Cl^-(50), Br^-(100), NO_3^-(100), SO_4^{2-}(100)
Neutralization capacity of dialysis device*	F^-(30), Cl^-(30), Br^-(60), NO_3^-(60), SO_4^{2-}(80)

* For this stage of the experiment, the mixture of anions was only diluted in 10^{-1} M NaOH.

Comparison of fibre types

Donnan dialysis was performed with 100 ml of camphorsulfonic acid and 100 ml of octanesulfonic acid at concentrations of 0.1 M, 0.5 M and 1.0 M. Dual ion-exchange was performed with slurry of 80 g of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200-400 mesh, in 25 ml of Milli-Q water.

Neutralization capacity of dialysis device

The neutralization capacity of the sample clean-up device was determined when the following hydrogen ion donating media were used :

1. 100 ml of 0.1 M octanesulfonic acid.
2. Slurry of 80 g of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200-400 mesh, in 25 ml of Milli-Q water.
3. Slurry of 80 g of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200-400 mesh, in 25 ml of 0.1 M octanesulfonic acid.
4. 100 ml of 0.45 M Millipore-Waters solid phase reagent SPR-H^+ -which is a solution of ultra fine (approximately 50nm in diameter) cation-exchange resin.

4.2.4 PROCEDURES

4.2.4.1 Comparison of hydrogen ion donating media

The cation-exchange hollow fibre was immersed in a hydrogen ion donating medium which was placed inside the glass tube as shown in Fig. 4.2. A 5 ml plastic syringe, which was connected to the inlet of the membrane, was used to pass 1 ml of each sodium hydroxide sample solution through the fibre. Pressure was applied to regulate the flow of sample through the membrane to approximately 1 ml/min. The first 10 drops of dialysate were discarded with the remaining volume of dialysate being collected in a small sample tube for ion chromatographic analysis. The pH of the samples was measured before and after dialysis using pH indicator sticks. Between experiments, the fibre was flushed thoroughly with Milli-Q water to

prevent carry-over from previous samples. The same procedure was repeated using various hydrogen ion donating media as listed in section 4.2.3.2.

4.2.4.2 Comparison of fibre types

The cation-exchange hollow fibre was coiled onto a holder of glass rods and placed inside the housing tube made from acrylic material as shown in Fig. 4.3. The inlet of the fibre was connected with the outlet of a Millipore-Waters M45 solvent delivery system by a 20 cm x 3 mm ID teflon tubing. The sodium hydroxide sample solution was passed through the fibre at a constant rate of 1 ml/min. The hydrogen ion donating solutions mentioned in section 4.2.3.2 were used in this experiment. Every 50 µl of dialysate was then analysed for its anion content by IC. This experiment was performed using the two different types of cation-exchange hollow fibres mentioned in section 4.2.2.

4.2.4.3 Neutralization capacity of dialysis device

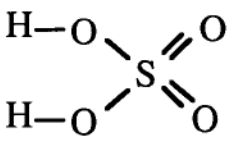
The dialysis device for the determination of neutralization capacity was the same as that used for the comparison of fibre types except that the hydrogen ion donating medium was stirred occasionally with a glass rod. The 0.1 M sodium hydroxide sample solution was continuously pumped through the hollow fibre at a constant rate of 1 ml/min. Dialysate was collected at regular intervals and at the same time the pH of the dialysate was monitored using pH indicator sticks until breakthrough of the sample occurred. Every 50 µl of collected dialysate was analysed by IC. The two types of fibres mentioned in section 4.2.2 (packed and unpacked fibre) and hydrogen ion donating media listed in section 4.2.3.2 were used in this experiment.

4.3 RESULTS AND DISCUSSION

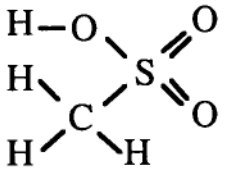
4.3.1 COMPARISON OF HYDROGEN ION DONATING MEDIA

The first step of this work was to determine the optimum composition of the hydrogen ion donating medium for a suitable sample treatment device. This was carried out by passing different concentrations of sodium hydroxide sample solutions through the dialysis device containing different types and concentrations of hydrogen ion donating media. The pH of the sample before and after dialysis was measured and the dialysed samples were examined for their anion content by IC. The hydrogen ion donating media used for this purpose were sulfuric acid, aliphatic sulfonic acids (MSA, OSA, CSA), aromatic sulfonic acid (TSA) and various hydrogen form cation-exchange resins (AG 50W-X8, AG 50W-X2, IRC-50, IR-120). These hydrogen ion donating media were chosen as they are readily available, common ion-exchangers. The chemical structures of the acid media are shown in Fig. 4.4.

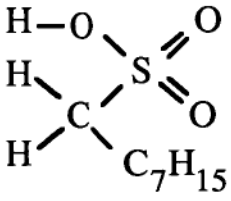
The measurement of pH of the dialysed sample showed that the pH was reduced during dialysis. Tables 4.2 to 4.5 show the changes in the pH of sodium hydroxide solutions after dialysis when various hydrogen ion donating media were employed. In all cases the pH of the sample was lowered significantly and the extent of pH reduction increased when the concentration of the hydrogen ion donating medium was increased. All of the sulfonic acids were more effective in lowering pH than sulfuric acid and some differences in performance between the different sulfonic acids can be noted, with octanesulfonic acid appearing to be the best medium for lowering the pH of sample solutions. The four cation-exchange resins used in the dual ion-exchange approach were less effective in lowering the sample pH; however, BioRad AG 50W-X8 gave the best performance. The various hydrogen ion donating media are compared in Figs. 4.5 to 4.8.



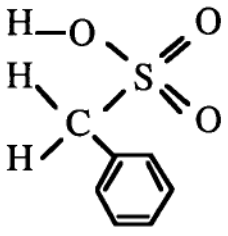
Sulfuric acid
MW = 98.1



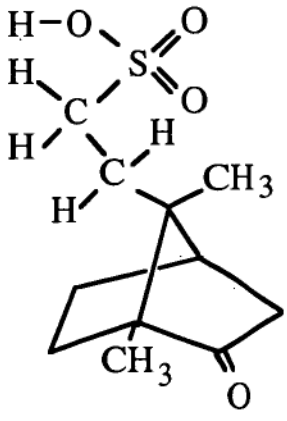
Methanesulfonic acid
MW = 96.1



Octanesulfonic acid
MW = 194.3



p-toluenesulfonic acid
MW = 190.2



Camphorsulfonic acid
MW = 232.3

Fig. 4.4 Chemical structures of hydrogen ion donating media.

TABLE 4.2
DIALYSATE pH FROM 10^{-1} M NaOH SAMPLES (pH = 13) USING VARIOUS HYDROGEN ION DONATING MEDIA.

	Hydrogen ion donating medium								
[M]	H_2SO_4	MSA	CSA	TSA	OSA	50W-X8	50W-X2	IRC-50	IR-120
0.1	12	11.5	11.5	11	10				
0.3	11	11.5	11	11	10				
0.5	11	11	11	10	9				
0.7	10.5	10	10	9	9				
1.0	10	10	10	9	9				
						10	10	11.5	11

TABLE 4.3
DIALYSATE pH FROM 10^{-2} M NaOH SAMPLES (pH = 12) USING VARIOUS HYDROGEN ION DONATING MEDIA.

	Hydrogen ion donating medium								
[M]	H_2SO_4	MSA	CSA	TSA	OSA	50W-X8	50W-X2	IRC-50	IR-120
0.1	8	7	7	7	7				
0.3	8	6	7	7	7				
0.5	7	5	7	6	6				
0.7	6	4	6	5	5				
1.0	6	4	5	4.5	5				
						7	7	8	10

TABLE 4.4
DIALYSATE pH FROM 10^{-3} M NaOH SAMPLES (pH = 11) USING VARIOUS HYDROGEN ION DONATING MEDIA.

	Hydrogen ion donating medium								
[M]	H_2SO_4	MSA	CSA	TSA	OSA	50W-X8	50W-X2	IRC-50	IR-120
0.1	5	4	5	5	5				
0.3	5	3	5	5	5				
0.5	5	3	5	4	4				
0.7	4.5	3	4	4	4				
1.0	4	3	4	3	4				
						4.5	4.5	5	5

TABLE 4.5
DIALYSATE pH FROM 10^{-4} M NaOH SAMPLES (pH = 10) USING VARIOUS HYDROGEN ION DONATING MEDIA.

	Hydrogen ion donating medium								
[M]	H_2SO_4	MSA	CSA	TSA	OSA	50W-X8	50W-X2	IRC-50	IR-120
0.1	4	4	5	4	3.5				
0.3	4	4	5	4	3.5				
0.5	3.5	4	4	3.5	3				
0.7	3.5	3	4	3	3				
1.0	3	3	3	3	3				
						4	4	4	4

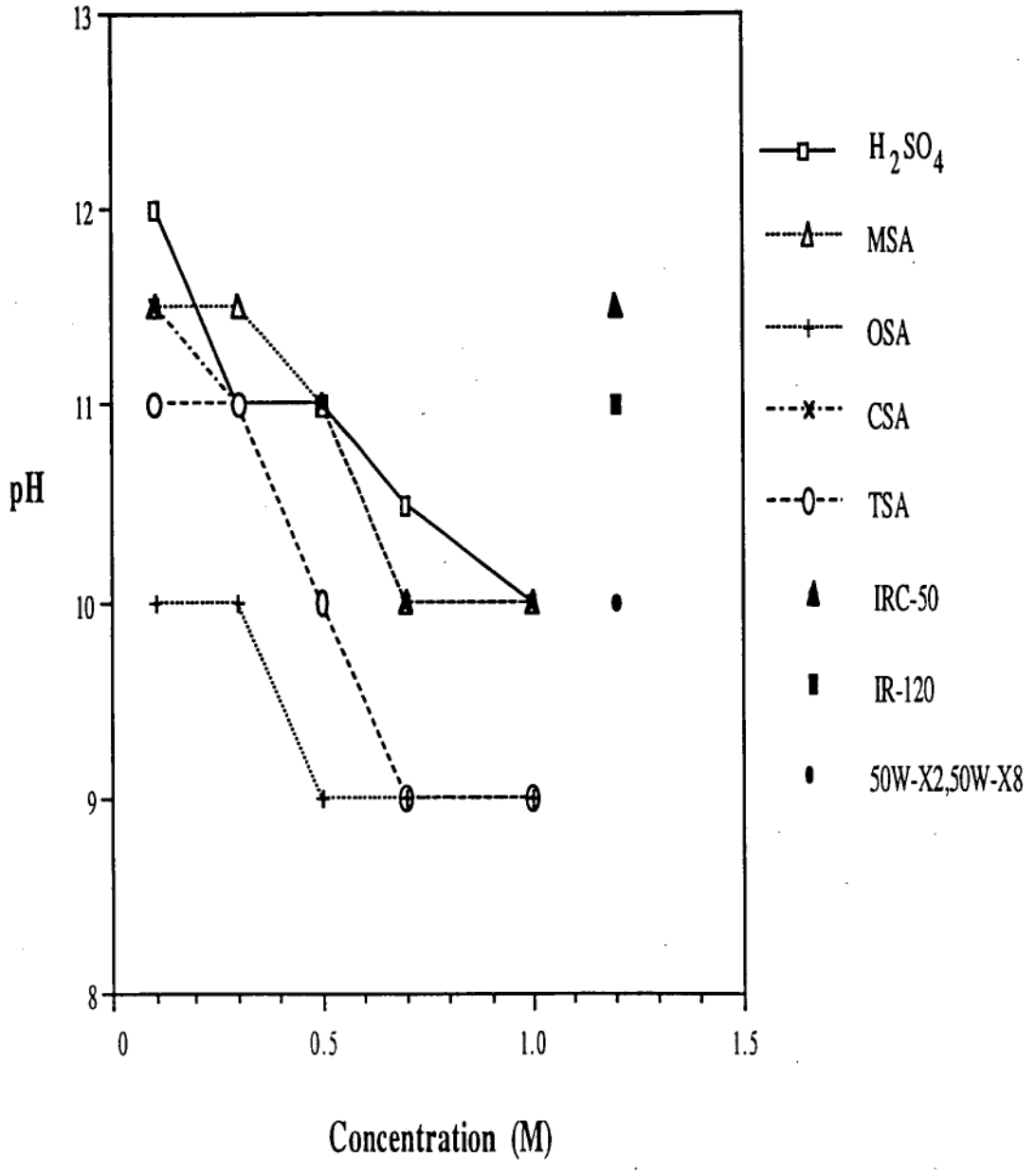


Fig. 4.5 pH of 10^{-1} M NaOH sample solutions after dialysis in various hydrogen ion donating media.

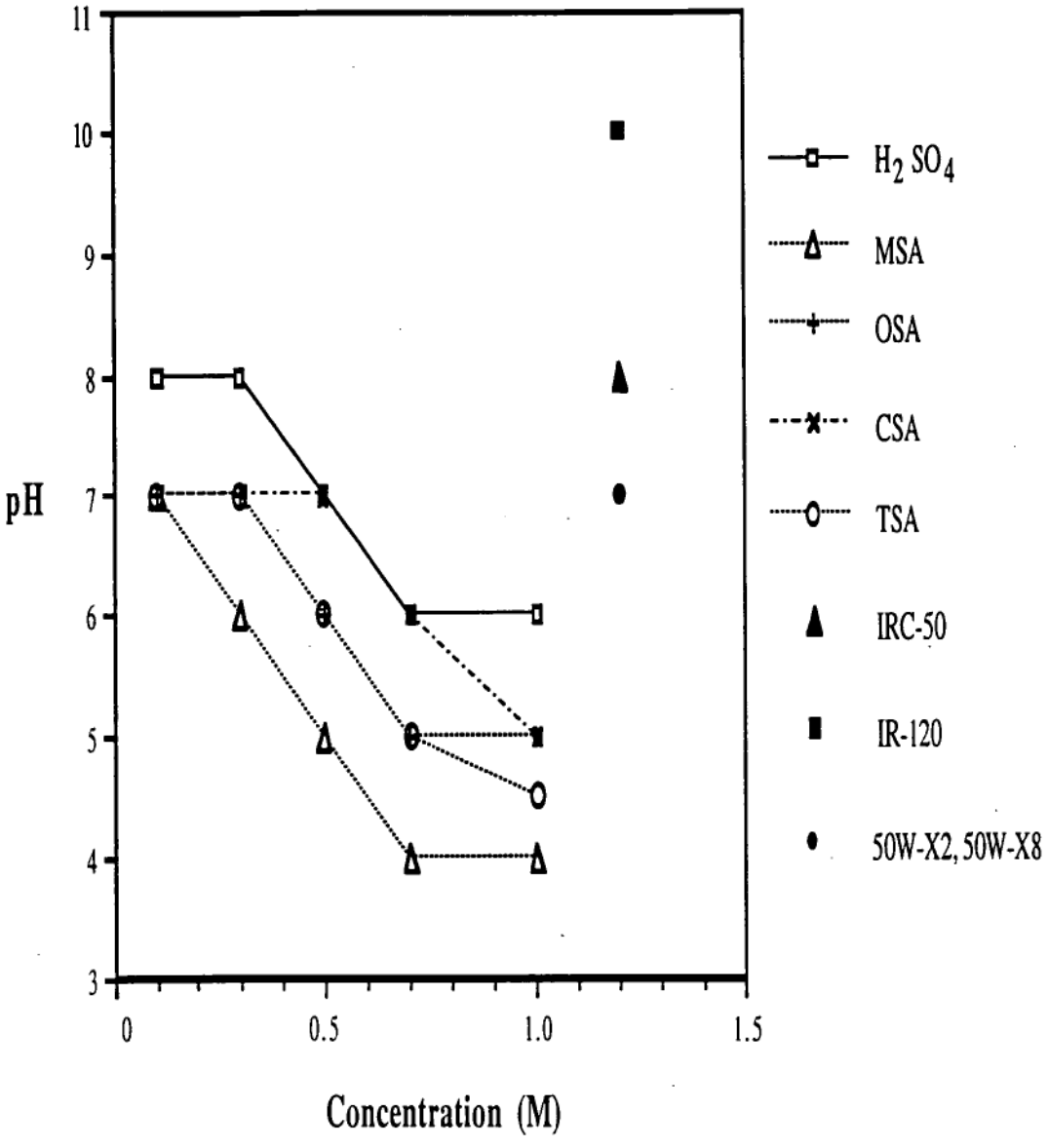


Fig. 4.6 pH of 10^{-2} M NaOH sample solutions after dialysis in various hydrogen ion donating media.

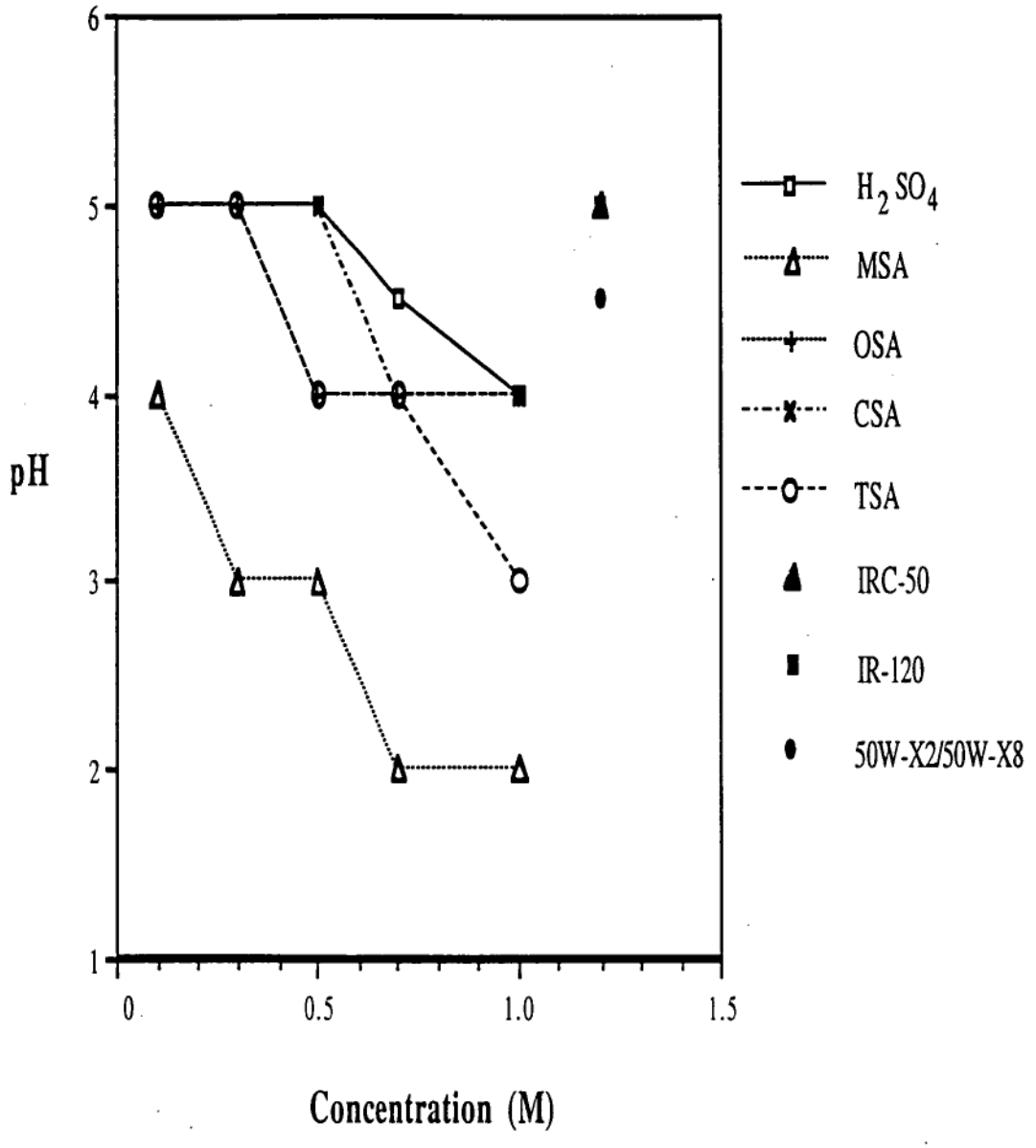


Fig. 4.7 pH of 10^{-3} M NaOH sample solutions after dialysis in various hydrogen ion donating media.

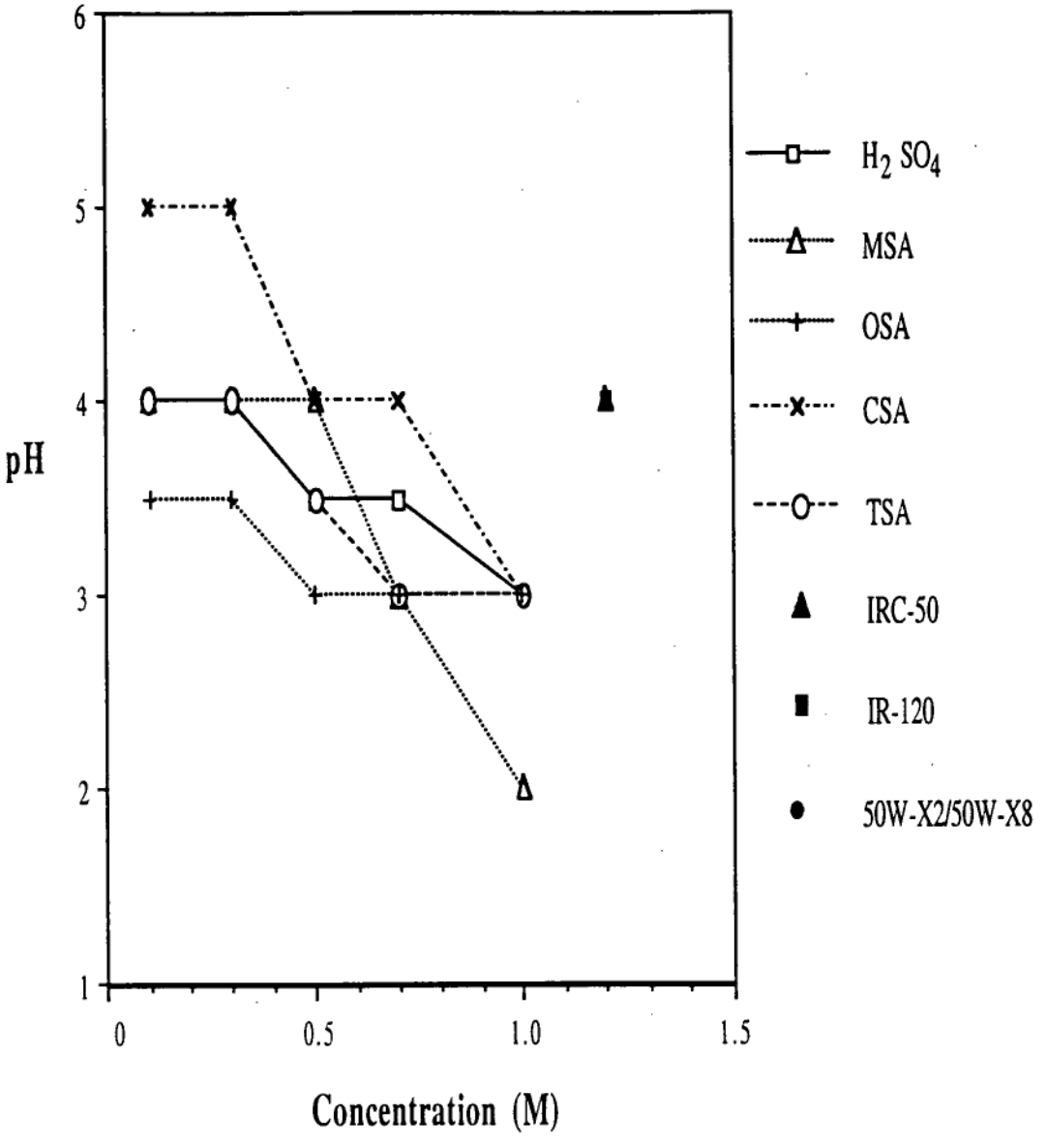


Fig. 4.8 pH of 10^{-4} M NaOH sample solutions after dialysis in various hydrogen ion donating media.

While using sulfuric acid as the hydrogen ion donating medium, it was noted that the sulfate ion penetrated the membrane, with the degree of sulfate incursion increasing with concentration of the sulfuric acid used as hydrogen ion donating medium. The diffusion of sulfate ion occurred due to the difference in the concentration gradient between the sample and hydrogen ion donating medium. Swelling of the sulfonated membrane also allowed penetration of sulfate ions to some extent. The transport of sulfate into the sample is also expected because of the non zero transport number for anions in a cation-exchange membrane [7]. Fig. 4.9 illustrates the contamination by sulfate ions during dialysis. The sulfate ions that entered the sample solutions were measured by their peak heights and were plotted against the concentrations of sulfuric acid used as the medium. The figure shows that the amount of sulfate which penetrated into the sodium hydroxide sample solutions was relatively independent of the concentration of the hydroxide solutions.

The clean-up device used in these experiments was capable of reducing the high ionic strength of the matrix and producing chromatograms with less distortion, in comparison to those obtained from samples not subjected to dialysis. In the latter case, the long recovery of the conductivity detector obscured the presence of inorganic anions when a sample solution of 10^{-1} M NaOH was injected to the ion chromatograph, whilst partially distorted chromatograms resulted when sample solutions of 10^{-2} M NaOH were analysed.

The chromatograms in Fig. 4.10 (a and b) show the effect of the high ionic strength of the matrix (10^{-2} M NaOH) prior to Donnan dialysis and after dialysis with 0.1 M octanesulfonic acid. The chromatogram after dialysis shows an improved baseline and less distortion of the peaks. The fluoride and chloride peaks are partially obscured prior to dialysis but can be quantitated after dialysis. The resolution of bromide and nitrate also appears to be better in the chromatogram after dialysis.

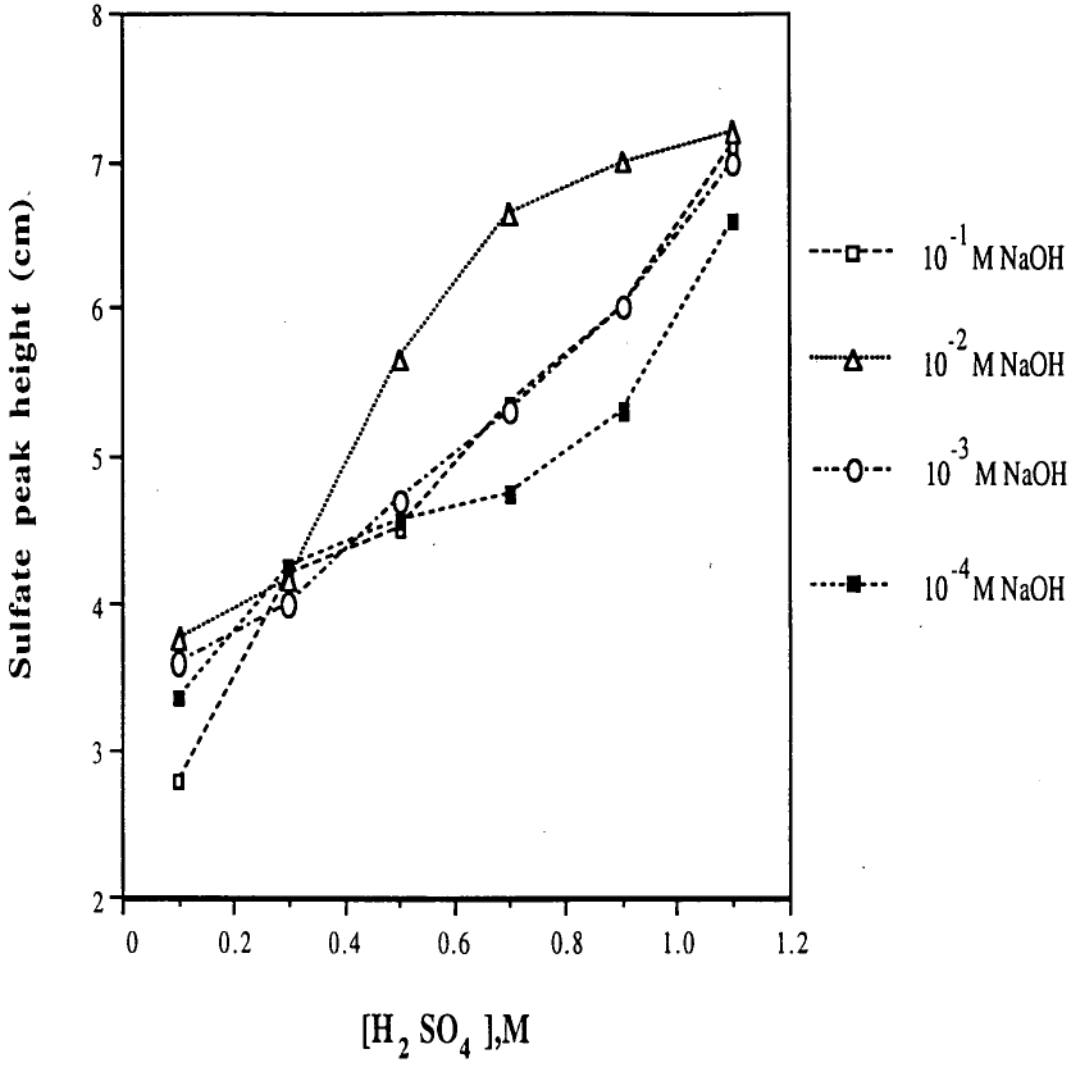


Fig. 4.9 Sulfate incursion into the sample from a H_2SO_4 medium after dialysis.

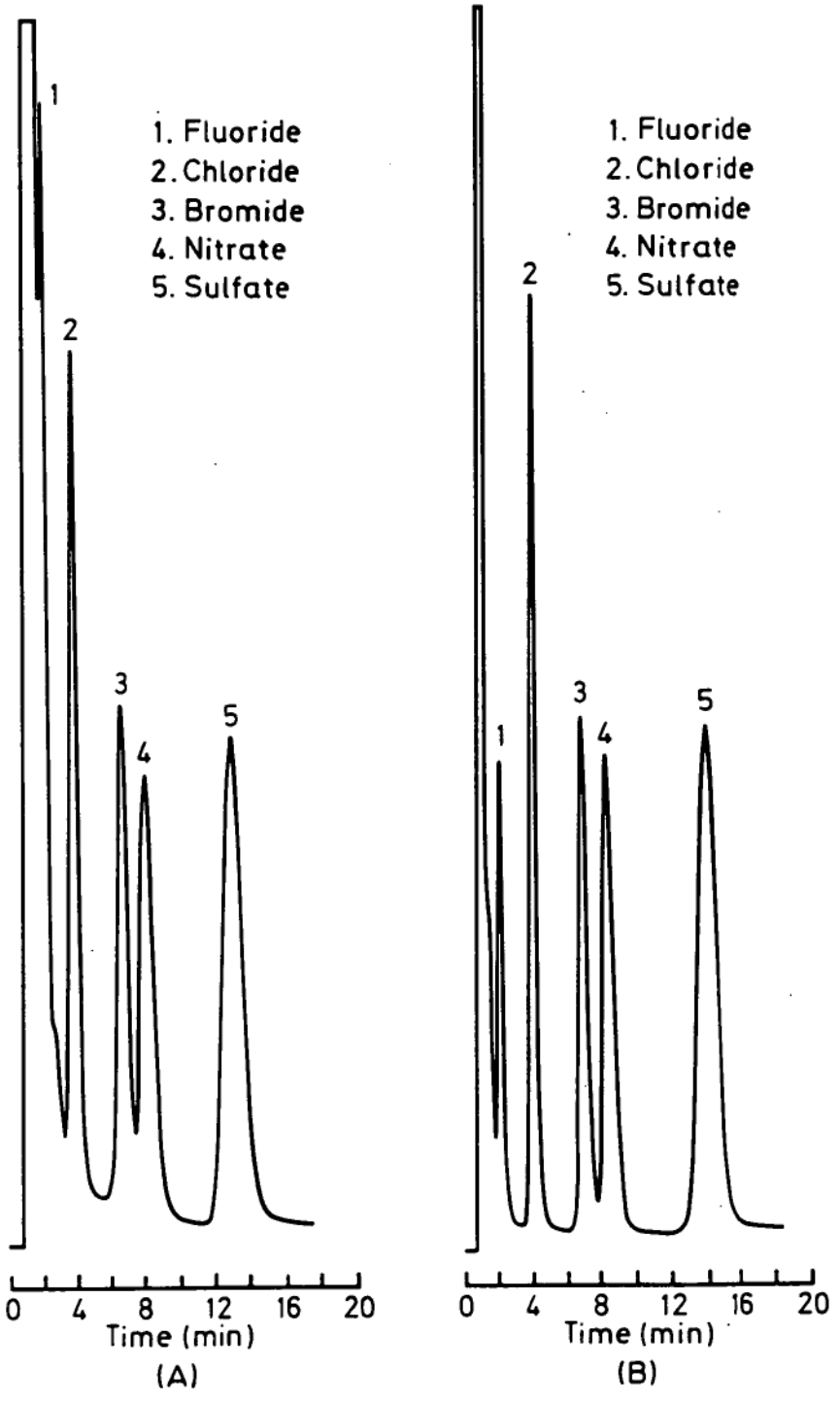


Fig. 4.10 Chromatogram obtained before (A) and after (B) Donnan dialysis of 10^{-2} M NaOH solution containing anions. Injection volume : 50 µl. Eluent : gluconate-borate, pH 8.5. Column : Waters IC Pak A, 50 x 4.6 mm ID.

Minimizing loss of analyte during dialysis is another important consideration of the experiment. The permselectivity of the cation-exchange hollow fibre is the main factor that determines the recovery of analyte anions in the sample solution. Table 4.6 shows the recovery of analyte anions (based on their peak heights) after dialysis compared with peak heights for the same analyte anions in Milli-Q water. The result shows that no significant loss of analyte occurred during the experiment. The fluoride present in the anion mixture in 10^{-1} M NaOH solution gave variable recoveries after dialysis with all hydrogen ion donating media; however, improved results were obtained after dialysis of 10^{-2} M, 10^{-3} M and 10^{-4} M NaOH solutions containing anions. For this reason, the recovery value for fluoride was higher than 100%. The high recoveries for sulfate when sulfuric acid was used as the hydrogen ion donating medium were due to penetration of sulfate through the membrane.

The incursion of the acid anion used in the dialysis are quite observable in some instances. At a concentration of more than 0.3 M, each of the sulfonic acids was found to penetrate the hollow fibre and enter the sample, with penetration of methanesulfonic acid being the most severe and octanesulfonic acid and camphorsulfonic acid showing least penetration. This is possibly due to the differences in their molecular weights. Sulfonic acids with high molecular weight (CSA, OSA) tend to show less penetration than acids with smaller molecular weight (TSA, MSA). Increasing the sulfonic acid concentration enhanced the penetration rate of the acid anion. However, there was not any noticeable difference in the degree of penetration of the acid anion between the aliphatic and aromatic sulfonic acid used in this experiment.

The chromatograms obtained using the acid anions as solutes are shown in Fig. 4.11. All gave similar negative peaks (indicating lower conductance than that of the gluconate borate eluent used), with the exception of methanesulfonic acid which produced a positive peak.

TABLE 4.6
AVERAGE RECOVERIES (%) OF SOLUTE ANIONS IN 10^{-1}-10^{-4} M NaOH AFTER DIALYSIS.
The range derived from 20 replicates is shown in parentheses.

Medium	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}
H_2SO_4	126 (4)	103 (14)	93 (18)	99 (14)	103 (18)	182 (77)
MSA	123 (55)	101 (19)	94 (8)	98 (19)	98 (17)	95 (9)
CSA	106 (28)	99 (14)	89 (15)	94 (8)	93 (19)	99 (9)
TSA	127 (62)	97 (14)	93 (10)	89 (14)	90 (7)	100 (11)
OSA	106 (38)	94 (12)	92 (8)	90 (5)	94 (11)	98 (10)
AG 50W-X8	116 (49)	96 (9)	93 (11)	102 (10)	95 (7)	89 (9)
AG 50W-X2	130 (44)	92 (9)	88 (8)	91 (10)	90 (6)	91 (12)
IRC-50	130 (78)	93 (13)	89 (18)	85 (16)	86 (12)	89 (12)
IR-120	118 (63)	90 (10)	90 (10)	86 (20)	85 (15)	88 (9)

Typical examples showing penetration of these acid anions into the sample solutions after dialysis are shown in Fig. 4.12. Severely distorted baselines for the dialysate chromatogram and obscuring of inorganic anion peaks can be noted. The fluoride peak is strongly distorted when the same acid anions are present in the dialysed sample, whilst the nitrite peak is totally absent from the chromatogram after dialysis with camphorsulfonic acid.

Dialysis using the dual ion-exchange process was performed using a slurry of cation-exchange resin in Milli-Q water. This process differs from Donnan dialysis with respect to the medium used, in that a cation-exchange resin slurry is used in place of an acid solution. The fixed sites of the cation-exchange resin are the co-ions and these are physically excluded from entering the sample by the cation-exchange membrane so that incursion into the sample is avoided. Changes in concentration of the analyte ion in the solution through contamination effects, adsorption losses or sample volume changes which commonly occur in conventional ion-exchange are also minimized. Tables 4.2 to 4.5 include the results obtained using cation-exchange resins for the neutralization of the sodium hydroxide sample solutions. From the four types of cation-exchange resins used, it was found that BioRad AG 50W-X8 is the most effective cation-exchange resin in lowering pH of the sample so this type of resin was employed in future studies.

4.3.2 COMPARISON OF FIBRE TYPES

Two types of cation-exchange hollow fibres (described in section 4.2.2) were used in this experiment and were placed in an acrylic housing as shown in Fig. 4.3. The sodium hydroxide solution containing inorganic anions was passed through the fibre using a Millipore-Waters M45 pump at a constant rate of 1 ml/min. From previous experiments, both octanesulfonic acid and camphorsulfonic acid were known to have minimum penetration through the membrane, so these two sulfonic acids and

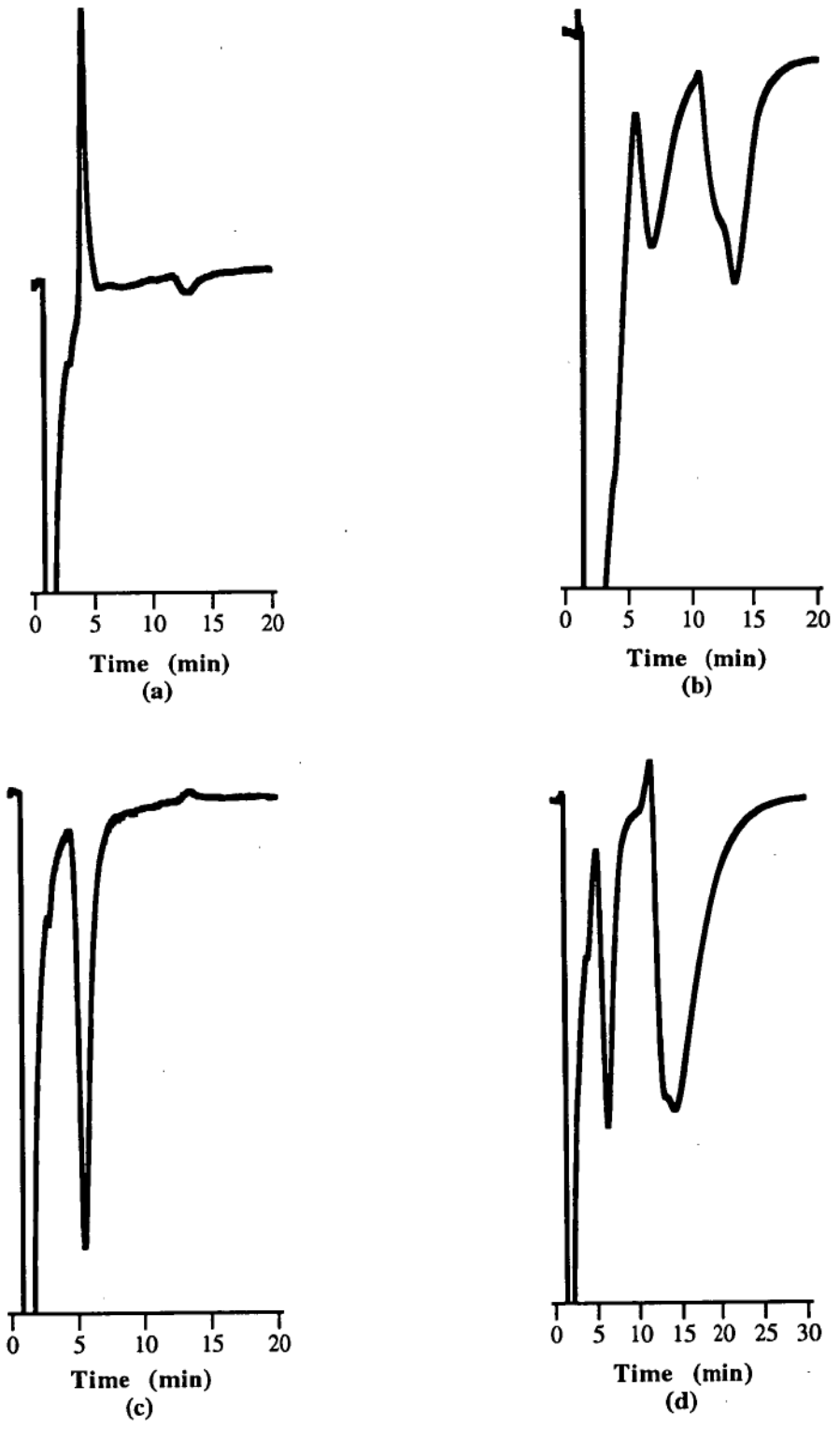


Fig. 4.11 Chromatograms of (a) methanesulfonic acid, (b) p-toluenesulfonic acid, (c) camphorsulfonic acid and (d) octanesulfonic acid as solutes. Concentration : 5 mM. Injection volume : 50 µl. Eluent : gluconate-borate, pH 8.5. Column : Waters IC Pak A, 50 x 4.6 mm ID.

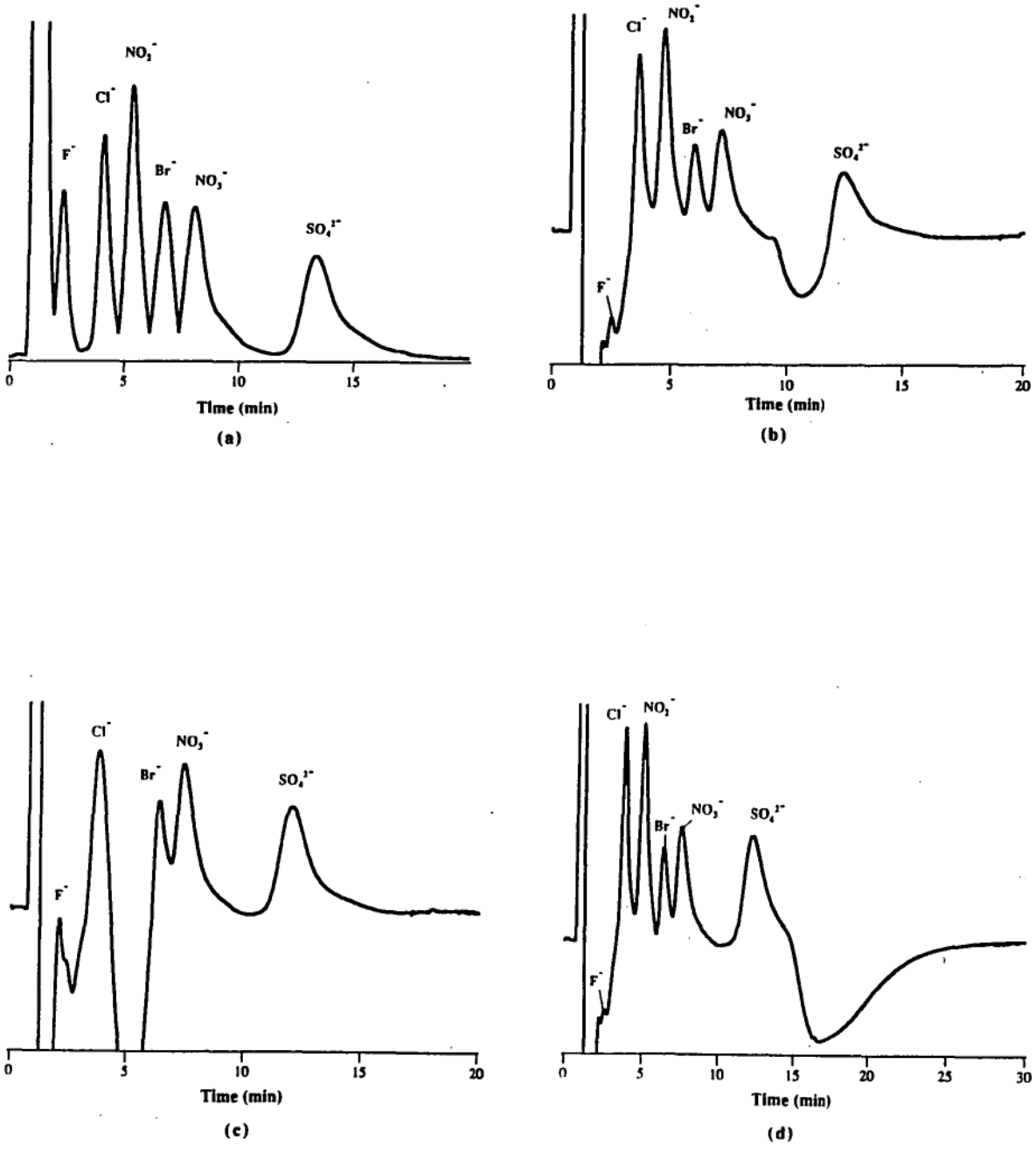


Fig. 4.12 Chromatograms of inorganic anions (a) in H_2O and showing penetration of (b) p-toluenesulfonic acid, (c) camphorsulfonic acid and (d) octanesulfonic acid. Injection volume : 50 µl. Eluent : gluconate-borate, pH 8.5. Column : Waters IC Pak A, 50 x 4.6 mm ID.

BioRad AG 50W-X8 hydrogen form cation-exchange resin were used as the hydrogen ion donating media for comparing the two types of cation-exchange fibres. The efficiency of the fibre in lowering the pH of the sample solutions and the degree of incursion of acid anion into the sample solution were examined.

The changes in pH of NaOH sample solutions using a 160 cm x 0.6 mm ID Nafion cation-exchange hollow fibre packed with polystyrenedivinylbenzene beads (packed fibre) are shown in Table 4.7. From the table, it can be seen that various concentrations of the hydrogen ion donating media have almost the same pH lowering effect on different concentrations of sodium hydroxide sample solutions. For example, 0.1 M camphorsulfonic acid and octanesulfonic acid and a slurry of BioRad AG 50W-X8 cation-exchange resin reduced the pH of all sample solutions to approximately 4. This result suggested that BioRad AG 50W-X8 cation-exchange resin has a similar capacity for lowering the pH of the sample solution as the 0.1 M sulfonic acid solutions. It was also noted that increasing the concentration of the acid medium resulted in only a slight reduction of sample pH. The table also shows that penetration of camphorsulfonic acid and octanesulfonic acid through the membrane occurred at a concentration of 0.5 M and higher. The degree of penetration increased with the concentration of the acid and the presence of the acid anion in the dialysed sample caused the distortion of the dialysate chromatogram as shown earlier in Fig. 4.12.

The second type of membrane used was a 345 cm x 0.5 mm ID unpacked Nafion cation-exchange hollow fibre (unpacked fibre) and the results of dialysis using various hydrogen ion donating media are tabulated in Table 4.8. From the table, it can be noted that each hydrogen ion donating medium gave a pH value of approximately 4 for all sodium hydroxide sample solutions. It appeared that the length of the membrane was such that the replacement of sodium ions in the sample

TABLE 4.7
DIALYSATE pH OF 10^{-1} M (pH=13), 10^{-2} M (pH=12), 10^{-3} M (pH=11) AND 10^{-4} M (pH=10) NaOH SAMPLES AFTER DIALYSIS USING PACKED NAFION FIBRE.

NaOH [M]	Hydrogen ion donating medium						
	CSA			OSA			AG 50W-X8
	0.1 M	0.5 M	1.0 M	0.1 M	0.5 M	1.0 M	
10^{-1}	4.0	3.5 / P	3.5 / P	4.5	3.5 / P	3.5 / P	4.5
10^{-2}	4.0	3.0 / P	3.0 / P	4.5	3.5 / P	3.5 / P	4.5
10^{-3}	4.0	3.0 / P	3.0 / P	4.0	3.5 / P	3.5 / P	4.0
10^{-4}	4.0	3.0 / P	3.0 / P	4.0	3.0 / P	3.0 / P	4.0

P = penetration of acid anion into the sample solution.

TABLE 4.8
DIALYSATE pH OF 10^{-1} M (pH=13), 10^{-2} M (pH=12), 10^{-3} M (pH=11) AND 10^{-4} M (pH=10) NaOH SAMPLES AFTER DIALYSIS USING UNPACKED NAFION FIBRE.

	Hydrogen ion donating medium						
NaOH [M]	CSA			OSA			AG 50W-X8
	0.1 M	0.5 M	1.0 M	0.1 M	0.5 M	1.0 M	
10^{-1}	4.0 / P	4.0 / P	3.5 / P	4.0	4.0 / P	3.5 / P	4.0
10^{-2}	4.0 / P	3.5 / P	3.0 / P	4.0	4.0 / P	3.5 / P	4.0
10^{-3}	4.0 / P	3.5 / P	3.0 / P	3.5	3.5 / P	3.0 / P	4.0
10^{-4}	4.0 / P	3.0 / P	3.0 / P	3.5	3.0 / P	3.0 / P	4.0

P = penetration of acid anion into the sample solution.

by hydrogen ions was maximized, so that higher concentrations of acid did not produce any further reduction in the pH of sample solution. Camphorsulfonic acid penetrated into the sample solution when used at concentrations of 0.1 M, 0.5 M and 1.0 M, whilst octanesulfonic acid showed similar behaviour at concentrations of 0.5 M and 1.0 M. These results indicated that camphorsulfonic acid was more mobile than octanesulfonic acid and penetrated membrane more easily.

The results above have shown that the packed fibre was the more efficient, since a 160 cm fibre of this type performed virtually identically to a 345 cm unpacked fibre in lowering the pH of sample solutions. It has also been shown that octanesulfonic acid is a more suitable hydrogen ion donating medium for Donnan dialysis than any other acid solution used in this experiment. The superior performance of the packed fibre is in accordance with the results obtained in previous studies using such fibres [8].

4.3.3 NEUTRALIZATION CAPACITY OF THE DIALYSIS DEVICE

Clean-up devices of the type described in this experiment will have a finite life (expressed as the volume of sample of known concentration which can be treated) governed by the volume and concentration of the hydrogen ion donating solution and the diffusion kinetics across the membrane. This lifetime can be determined using breakthrough experiments by measuring the pH of the dialysate and noting the volume of sample which may be treated until the pH of the effluent shows a rapid increase.

Fig. 4.13 shows the breakthrough curve for the 160 cm packed fibre and the 345 cm unpacked fibre using 100 ml of 0.1 M octanesulfonic acid as hydrogen ion donating medium and 0.1 M sodium hydroxide solution containing anions as sample.

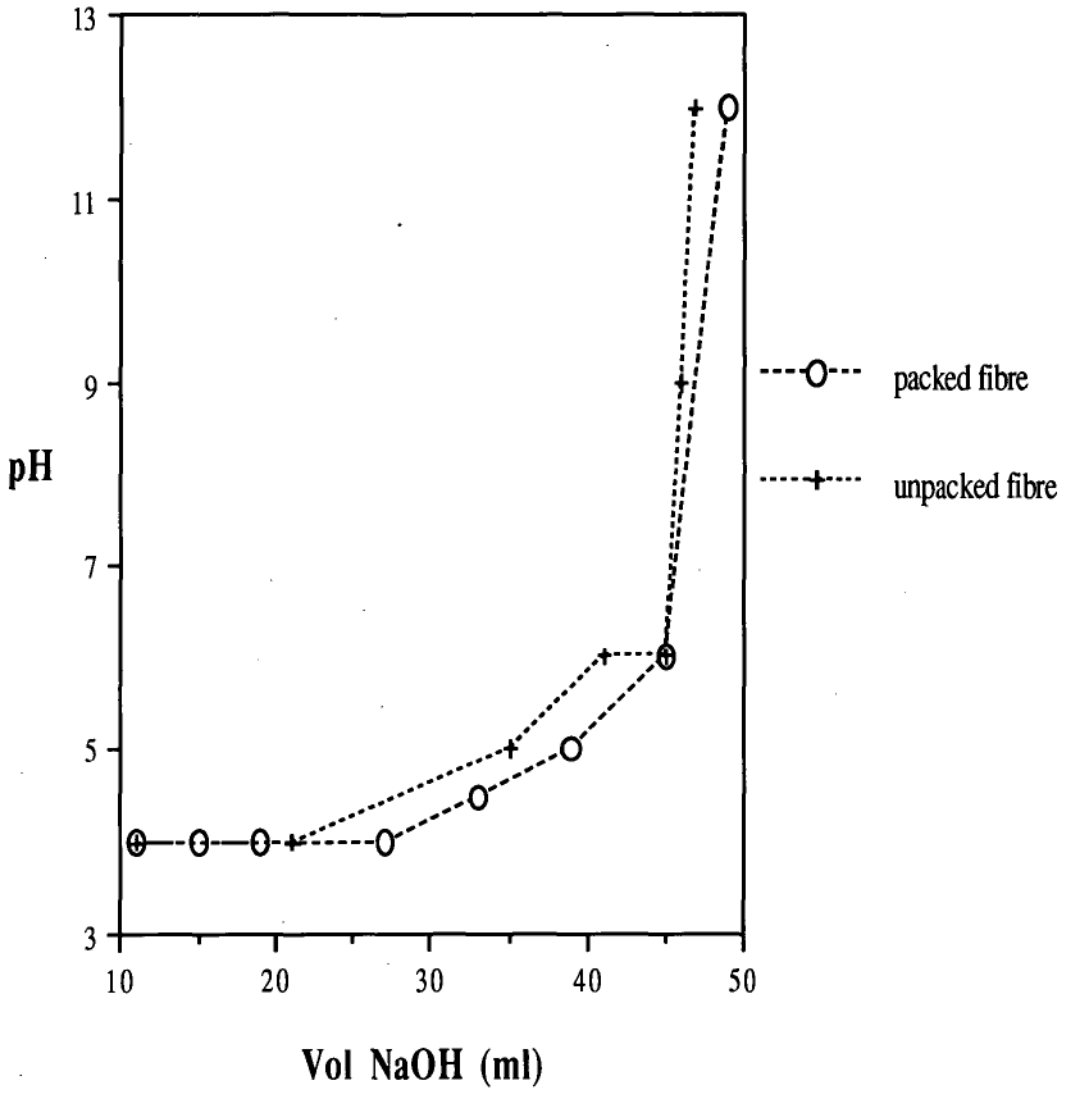


Fig. 4.13 Breakthrough curve for the packed fibre and unpacked fibre using 100 ml of 0.1 M octanesulfonic acid as hydrogen ion donating medium and 10^{-1} M NaOH as sample.

In both cases, the breakthrough point occurred after 47 ml of sample solution passed through the membrane. This neutralization capacity corresponds to 47 percent of the total theoretical capacity of the device (calculated by assuming that all of the hydrogen ions in the hydrogen ion donating medium are available to neutralize the sample).

The neutralization capacity cannot be increased substantially simply by increasing the concentration of hydrogen ion donating medium because of the likelihood of penetration of the acid anion, even when OSA is used. However, resin slurries offer very high theoretical neutralization capacities. For example, direct titration of 5 g of BioRad AG 50W-X8 cation-exchange resin with 0.1 M NaOH using a phenolphthalein indicator gave an end-point corresponding to 127.5 ml of NaOH. A slurry containing 80 g of resin therefore has a theoretical total neutralization capacity corresponding to 2040 ml of 0.1 M NaOH.

A slurry of BioRad AG 50W-X8 cation-exchange resin (80 g in 25 ml of Milli-Q water) was used as the hydrogen ion donating medium and the breakthrough of this medium occurred after 25 ml of 0.1 M NaOH solution had passed through the device. This low breakthrough point suggested that the transfer of hydrogen ions from one resin particle to the next and ultimately through the membrane is rather slow when water is used as the slurrying solvent. One possible solution to this problem is to use an acid solution as the slurrying solvent, at a concentration below which penetration of the acid anion through the membrane occurs. The same amount of resin slurried in 25 ml of 0.1 M octanesulfonic acid used as the medium showed a breakthrough point at 300 ml, which is an increase by a factor of 12. However, this neutralization capacity is only approximately 15% of the theoretical total of the hydrogen ions contained in the resin and the octanesulfonic acid slurrying solvent.

The performance of the resin slurry was improved greatly by occasional stirring. The breakthrough point was 1800 ml for the packed fibre and 2000 ml for the unpacked fibre, the latter value corresponding to 98% of the theoretical capacity value. *In situ* regeneration of the exhausted resin was attempted by passing 50 ml of 1 M octanesulfonic acid through the resin. Further use of the regenerated resin slurry gave breakthrough points of 600 ml and 450 ml for the packed fibre and unpacked fibre, respectively. Although some neutralization capacity was restored after the regeneration of the exhausted resin, the original performance was not recovered, suggesting that more thorough regeneration was necessary. Table 4.9 shows the neutralization capacities obtained with a number of resin slurries with the two types of fibres. Data for the packed fibre showed similar trends but in each case the neutralization capacities were less than those for the unpacked fibre, presumably due to the shorter length of the former.

The particle size of the resin is also likely to exert some influence on performance. This aspect was not studied in detail; however a solution of ultra-fine (approximately 50 nm in diameter) cation-exchange resin was examined as a hydrogen ion donating medium. The particular reagent used was Millipore-Waters SPR-H^+ reagent, which has been used for post-column addition to IC eluents as a means of reducing their conductance through protonation reactions [9]. When titrated with base, this solution was found to contain 0.45 M of H^+, so that 100 ml provides a theoretical neutralization capacity corresponding to 4.5 l of 0.1 M NaOH. As shown in Table 4.9, the SPR-H^+ reagent gave a low neutralization capacity (approximately 5% of the theoretical value), even when the solution was stirred. Examination of the fibre by electron microscopy after use of the SPR-H^+ reagent showed particles of resin imbedded in the pores of the fibre, suggesting that physical blockage of the fibre could be responsible for the observed low neutralization capacity.

TABLE 4.9
NEUTRALIZATION CAPACITY ACHIEVED WITH VARIOUS HYDROGEN ION DONATING MEDIA.

Hydrogen ion donating medium	Volume 10^{-1} M NaOH neutralized	
	Unpacked fibre	Packed fibre
A	47 ml	47 ml
B	25 ml	n.m.
C	300 ml	n.m.
D	2000 ml	1800 ml
E	450 ml	600 ml
F	220 ml	0 ml

n.m. = not measured.

A = 100 ml of 0.1 M octanesulfonic acid.

B = 80 g of BioRad AG 50W-X8 in 25 ml of Milli-Q water, without stirring.

C = 80 g of BioRad AG 50W-X8 in 25 ml of 0.1 M octanesulfonic acid, without stirring.

D = 80 g of BioRad AG 50W-X8 in 25 ml of 0.1 M octanesulfonic acid, stirred.

E = regenerated D with 50 ml of 1.0 M octanesulfonic acid.

F = 100 ml of 0.45 M SPR-H^+ reagent.

4.4 CONCLUSIONS

This study has shown that clean-up of strongly alkaline samples prior to ion chromatographic analysis can be achieved with the aid of membrane fibre devices. The hydrogen ion donating solution into which the fibre is immersed must be chosen carefully to avoid penetration of the acid anion into the sample. Hydrophobic sulfonic acids, such as octanesulfonic acid and camphorsulfonic acid give best results. The neutralization capacity of the clean-up devices can be increased greatly by using a slurry of cation-exchange resin in the hydrogen form as the hydrogen ion donating medium. If a suitable acid (such as 0.1 M octanesulfonic acid) is used as the slurrying solvent and the slurry is stirred during use, the neutralization capacity approximates the theoretical maximum value dictated by the total ion-exchange capacity of the resin.

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CHAPTER FIVE

A STUDY OF ELECTROMIGRATION OF INORGANIC ANIONS USING AN "ELUTRAP" APPARATUS

5.1 INTRODUCTION

Ion chromatographic techniques generally give best results when applied to samples with a solute concentration greater than 1 μg/ml. Below this concentration level, either larger injection volumes must be employed or a sample preconcentration method is necessary. The most widely applicable of these methods involves the use of a specialty precolumn designed to trap trace levels of solutes from a large volume of sample. The precolumn method is popular because it is amenable to automation, offers high enrichment factors, and is less prone to sample contamination effects than other methods [1, 2]. Nevertheless, the technique is a complex procedure and suffers from the disadvantage of matrix dependence [3].

Trace enrichment can also be performed by Donnan dialysis, in which solute ions are transferred from the sample to a receiving electrolyte solution *via* an ion-exchange membrane. The use of Donnan dialysis for preconcentration of both anions and cations has been reviewed earlier in Chapter 2. This method usually requires some important additional steps before the receiver solution can be injected onto an IC and this is mainly due to the high ionic strength of the receiver. Although Donnan dialysis offers useful preconcentration, its application in IC is still limited because of constraints on the nature of the receiver solution and the eluent to be used for the final IC analysis. The need for a simple trace enrichment method is therefore evident.

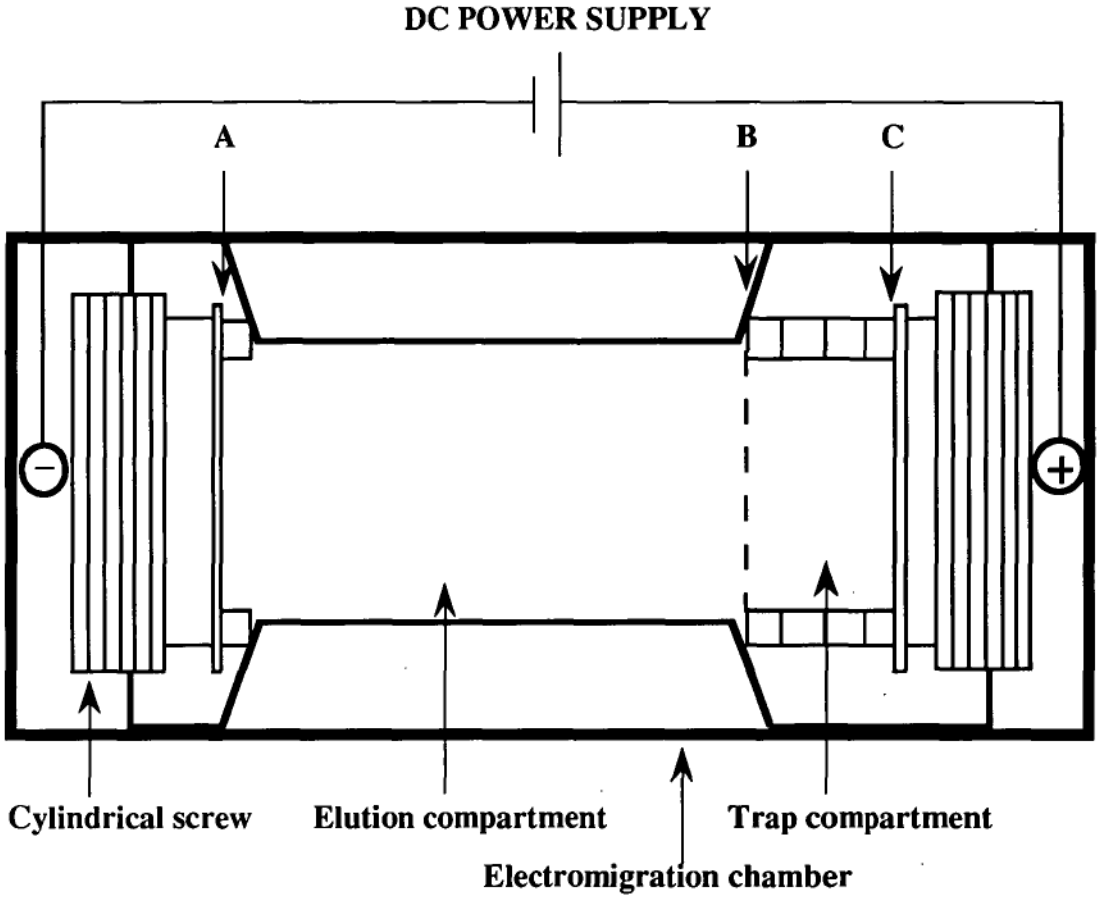
In this work, a preliminary study into the utility of an "Elutrap" apparatus for sample

enrichment and clean-up in anion IC was conducted. Selective removal of anions using two different types of membranes was anticipated and at the same time, the "Elutrap" was used to study the migration pattern of common inorganic anions in an aqueous solution under a constant applied potential.

"Elutrap" (Schleicher & Schuell, Inc., Keene, NH, USA) is an electrophoretic device designed for purification and concentration of charged macromolecules by filtration under an electrical field. The device, depicted schematically in Fig 5.1, is made from a polycarbonate block (160 x 30 x 30 mm) with an open channel (width 12 mm, depth 22 mm) along its longitudinal axis which is divided into two compartments by three planar membranes. Two types of membranes differing in their pore sizes are utilized in this device, namely membrane BT1 and membrane BT2 , with the latter having the larger pore size. An elution compartment is formed by inserting two membranes at position A and B, and a "trap" compartment is located between the membranes positioned at B and C (as shown in Fig. 5.1). The membranes are inserted from above and held in place by the pressure of two hollow cylindrical screws.

The device is usually placed in a horizontal electrophoresis chamber filled with buffer and the electrophoretic process is carried out by applying an electrical potential across the chamber. Sample molecules initially added to the elution compartment will migrate through membrane B into the trap formed between membranes B and C. The first membrane in the trap (B) compartment acts as a prefilter which excludes large particles and other contaminants, whilst the second membrane (C) retains smaller sample molecules inside the trap. Both membranes allow the passage of buffer in the electrical field but in the absence of current, the volume in the trap remains constant.

The "Elutrap" facilitates the elution of proteins and DNA from gels, the concentration of dilute solutions, and the removal of salts and contaminating particles without denaturation or loss of sample material due to surface adsorption [4]. The apparatus is



A, B and C are positions of membrane

Fig. 5.1 "Elutrap" electromigration cell.

particularly valuable for processing small volumes or for isolating small quantities of material and it has been employed for an electroelution of five different membrane proteins from preparative sodium dodecylsulfate-polyacrylamide gels [5]. This work has shown that the "Elutrap" is easier to handle and has produced better recovery and reproducibility than some other electrophoretic devices.

In the present work, the elution compartment was filled with mixture of inorganic anions in Milli-Q water and the trap was filled with Milli-Q water to the same level. The device was placed in a home made electromigration chamber filled with Milli-Q water. Different constant potentials were applied between platinum wire electrodes at the two ends of the electromigration chamber. The anions were expected to migrate from the elution compartment toward the positive electrode and the membranes that form the trap compartment were expected to selectively prevent the anions from entering the electrode solution. Cations will migrate toward the negative electrode. During the migration process, a small amount of sample from different compartments was taken for determination of their anionic concentrations by non-suppressed IC.

5.2 EXPERIMENTAL

5.2.1 INSTRUMENTATION

The ion chromatographic system consisted of a Millipore-Waters (Milford, MA, USA) model 510 pump, model U6K injector and model 430 conductivity detector. The column used was a Millipore-Waters IC Pak A anion-exchange column, 50 x 4.6 mm ID, packed with polymethacrylate anion-exchange resin and the chromatography was carried out at room temperature with an eluent flow-rate of 1.2 ml/min. Chromatograms were recorded on a Cole Parmer (Chicago, Illinois, USA) chart recorder and on a Millipore-Waters Maxima 820 data station.

The electromigration cell used in this work (shown in Fig. 5.1) was connected with the trap compartment pointing to the positive electrode. Electrodes were constructed from platinum wires (60 x 0.25 mm OD), clipped to the cell and connected to a BioRad (Richmond, CA, USA) microprocessor-controlled electrophoresis power supply (model 3000 Xi).

5.2.2 REAGENTS AND STANDARD SOLUTIONS

Water purified using a Millipore (Bedford, MA, USA) Milli-Q water purification system was used for all solutions and all chemicals used were of analytical reagent grade. Samples and eluents were prepared daily, filtered through a Millipore 0.45 µm membrane filter and degassed in an ultrasonic bath prior to use. The eluent used for IC analysis of the treated samples contained 1.3 mM sodium tetraborate, 5.8 mM boric acid and 1.4 mM potassium gluconate adjusted to pH 8.5 and made up in water:acetonitrile (88:12, v/v).

Standard stock solutions of inorganic anions were prepared by dissolving appropriate amounts of sodium salts in Milli-Q water. Working solutions of these ions were obtained by diluting the stock solutions in Milli-Q water to give a mixture of F^- (30 µg/ml), Cl^- (30 µg/ml), Br^- (60 µg/ml), NO_3^- (60 µg/ml) and SO_4^{2-} (80 µg/ml).

5.2.3 PROCEDURES

The "Elutrap" was assembled with BT1 membranes inserted at position A and at position C, and a BT2 membrane at position B. The elution compartment was filled with 5 ml of a mixture of anions (as listed above) in Milli-Q water and the trap was filled with 2 ml of Milli-Q water. The device was placed in the electromigration chamber filled with 100 ml of Milli-Q water and constant potentials of 400 V, 500 V and 600 V were applied . During the migration process, 10 µl aliquots were

removed from the elution compartment (sample A) and the trap compartment (sample B) at intervals of 30 min and were assayed for their anion concentration.

The effects of different arrangements of the membranes were examined at a constant potential of 500 V with (a) BT1 membranes inserted at position A, B and C, and (b) BT2 membranes inserted at position A, B and C.

5.3 RESULTS AND DISCUSSION

5.3.1 EFFECT OF APPLIED POTENTIAL

In the presence of an electrical potential, anions in an aqueous solution migrate toward the positive electrode and cations move toward the negative electrode. The velocity of these ions under a unit potential gradient is termed the ionic mobility. An anion with a higher ionic mobility value travels toward the positive electrode faster than a less mobile anion. Ionic mobility is usually expressed in $volt^{-1}$ sec^{-1} $equiv^{-1}$ cm^2 and the values for some common inorganic anions are given in Table 5.1. The ionic mobility of a given ionic species is characteristic and depends on external conditions, e.g. temperature, pressure, and concentration.

In a migration device with compartments separated by membranes, as employed in this study, the migration of ions is not governed solely by their ionic mobilities. The solvated (or hydrated) size of solute ion exerts a significant interaction with the pore of the membrane, with ions of smaller solvated size showing greater ease of migration through the membrane than ions with a larger solvated size. The ionic radius of the solute ion also has a similar effect.

In this work, two types of membranes (which are supplied with the "Elutrap" by the manufacturer) were employed. BT1 membranes were placed at positions A and C as

TABLE 5.1

PHYSICAL PROPERTIES OF INORGANIC ANIONS [6, 7].

Anions	Charge/mass ratio	Ionic mobility at 25^0 C ($volt^{-1}$ sec^{-1} $equiv^{-1}$ cm^2)	Ionic radius (nm)	Hydrated ionic radius (nm)
OH^-	0.059	197.2	n.a.	n.a.
SO_4^{2-}	0.020	80.8	0.156	0.379
Br^-	0.013	78.1	0.206	0.330
I^-	0.019	76.5	0.235	0.331
Cl^-	0.028	76.4	0.182	0.332
NO_2^-	0.022	71.8	n.a.	n.a.
NO_3^-	0.016	71.4	0.206	0.335
F^-	0.053	54.4	0.136	0.352

n.a. = data not available.

shown in Fig. 5.1 and were expected to selectively prevent the anions from migrating to the electrode area. A BT2 membrane, having a larger pore size, was placed at position B and acted as a prefilter to prevent larger anions from entering the trap compartment. Constant potential was applied to the electromigration process to provide the driving force for anions to migrate towards the positive electrode. Under these conditions, larger sized and less mobile anions were expected to be retained longer inside the elution compartment, whilst the smaller, more mobile anions would be trapped inside the trap compartment. When the potential is switched off, the membranes do not permit further migration of anions. Fig. 5.2 illustrates the migration of ions during the electromigration process. In this diagram, a mixture of different sized cations and anions was present initially in the elution compartment. Under applied potential, small sized cations migrate through the BT1 membrane toward the negative electrode area and large sized cations are unable to pass through the membrane since the pore size of the membrane is smaller than the size of the cations. A similar effect occurs for the large sized anions which are prevented from migrating toward the positive electrode by the BT2 membrane. Smaller sized anions are able to pass through the BT2 membrane, but some of the larger sized anions are stopped from migrating further by the BT1 membrane. The smallest sized anions are permitted to migrate to the positive electrode area. A migration pattern of inorganic anions is therefore expected to occur due to the differences in their sizes.

A convenient method for assessing the migration pattern of the anions during the process is to analyse the anion content of the various solutions. This was carried out by injecting a small fraction of the sample solution from the elution compartment (sample A) and from the trap compartment (sample B) onto an ion chromatograph. The amount of anions present in both compartments is expressed as a percentage of the total anion present in the original sample solution. The results obtained by applying constant potentials of 400 V, 500 V and 600 V are given in Tables 5.2 to 5.4 respectively.

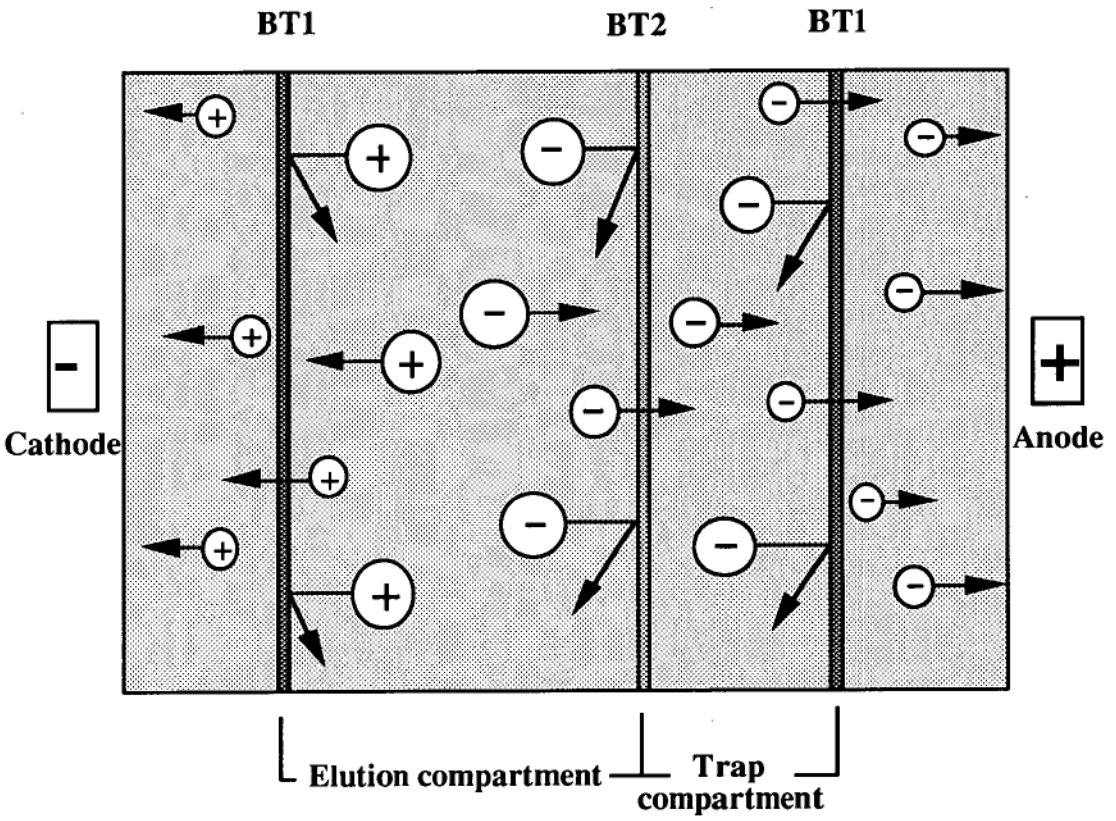


Fig. 5.2 Schematic diagram of the electromigration process.

TABLE 5.2
PERCENTAGE OF ANIONS PRESENT IN THE ELUTION COMPARTMENT (A) AND IN THE TRAP COMPARTMENT (B) AT DIFFERENT TIMES USING A CONSTANT POTENTIAL OF 400 V.

	F^-		Cl^-		Br^-		NO_3^-		SO_4^{2-}	
Minute	A	B	A	B	A	B	A	B	A	B
0	100	0	100	0	100	0	100	0	100	0
30	95.1	2.3	88.1	6.4	88.9	6.3	93.5	6.1	90.1	7.1
60	67.0	8.0	13.0	12.8	8.1	12.4	9.3	17.6	10.1	15.8
90	32.7	25.6	6.3	1.9	0	1.8	3.3	3.9	4.6	3.1
120	23.3	13.0	5.0	1.5	0	0	2.2	0.9	3.0	1.0
150	1.6	3.0	2.3	1.1	0	0	0	0.3	0	0.6

TABLE 5.3
PERCENTAGE OF ANIONS PRESENT IN THE ELUTION COMPARTMENT (A) AND IN THE TRAP COMPARTMENT (B) AT DIFFERENT TIMES USING A CONSTANT POTENTIAL OF 500 V.

	F^-		Cl^-		Br^-		NO_3^-		SO_4^{2-}	
Minute	A	B	A	B	A	B	A	B	A	B
0	100	0	100	0	100	0	100	0	100	0
30	90.4	3.1	84.9	7.1	77.6	7.5	90.3	7.2	81.6	8.6
60	50.0	21.6	12.7	4.6	2.8	6.4	6.7	6.7	3.1	9.6
90	12.1	23.5	5.7	0	0	0	0	0	1.9	0
120	11.2	9.8	2.7	0	0	0	0	0	1.3	0
150	0.8	1.3	0.6	0	0	0	0	0	0	0

TABLE 5.4
PERCENTAGE OF ANIONS PRESENT IN THE ELUTION COMPARTMENT (A) AND IN THE TRAP COMPARTMENT (B) AT DIFFERENT TIMES USING A CONSTANT POTENTIAL OF 600 V.

	F^-		Cl^-		Br^-		NO_3^-		SO_4^{2-}	
Minute	A	B	A	B	A	B	A	B	A	B
0	100	0	100	0	100	0	100	0	100	0
30	77.8	4.2	61.9	10.7	55.2	10.3	68.2	11.1	72.6	14.2
60	21.7	24.4	9.7	7.0	0	4.0	0	6.0	0	8.0
90	6.8	2.9	4.0	0	0	0	0	0	0	0
120	4.4	2.0	0	0	0	0	0	0	0	0
150	0.2	0.7	0	0	0	0	0	0	0	0

From Table 5.2, it can be noted that after 30 min of the electromigration process, the diffusion of different anions through the BT2 membrane occurred at similar rates. This was shown by the amount of anions remaining in the elution compartment, which were in the range of 88-95%, with small quantities of the anions present in the trap compartment. The amount of anions in the elution compartment was greatly reduced after 60 min of the process, whilst fluoride appeared to be the least mobile anion, since its level in the elution compartment was higher than for other anions. It was noted that the migration order of anions was not established clearly at this stage of the process. However, after 90 min the anions showed a migration order as follows : $Br^- > NO_3^- > SO_4^{2-} > Cl^- > F^-$. It was also noted that a longer time permits the anions to migrate totally to the anode area, with the exception of fluoride and chloride which were still present in the elution compartment.

The effect of applying 500 V to the system is given in Table 5.3. A similar result to that at 400 V was obtained. However, the migration rate of the anions toward the anode increased with the applied potential. This trend was also apparent when a constant potential of 600 V was applied, giving the results listed in Table 5.4. This table indicates that most of the anions had migrated from the elution compartment after 90 min, with the exception of fluoride and chloride. After 120 min, a small amount of fluoride was still present both in the elution and trap compartments, while other anions had been completely removed from both compartments. The increase in applied potential therefore resulted in a faster migration rate for all ions. The effect of applied potential on migration of anions is illustrated by plotting the applied potentials against the percentage of anions present in both compartments and are shown in Figs. 5.3 and 5.4, respectively.

It was observed that the amount of anions in the trap compartment during the electromigration process did not exceed 25% of the total and in most cases the percentage started to decrease after 60 min. Moreover, the total percentage of anions

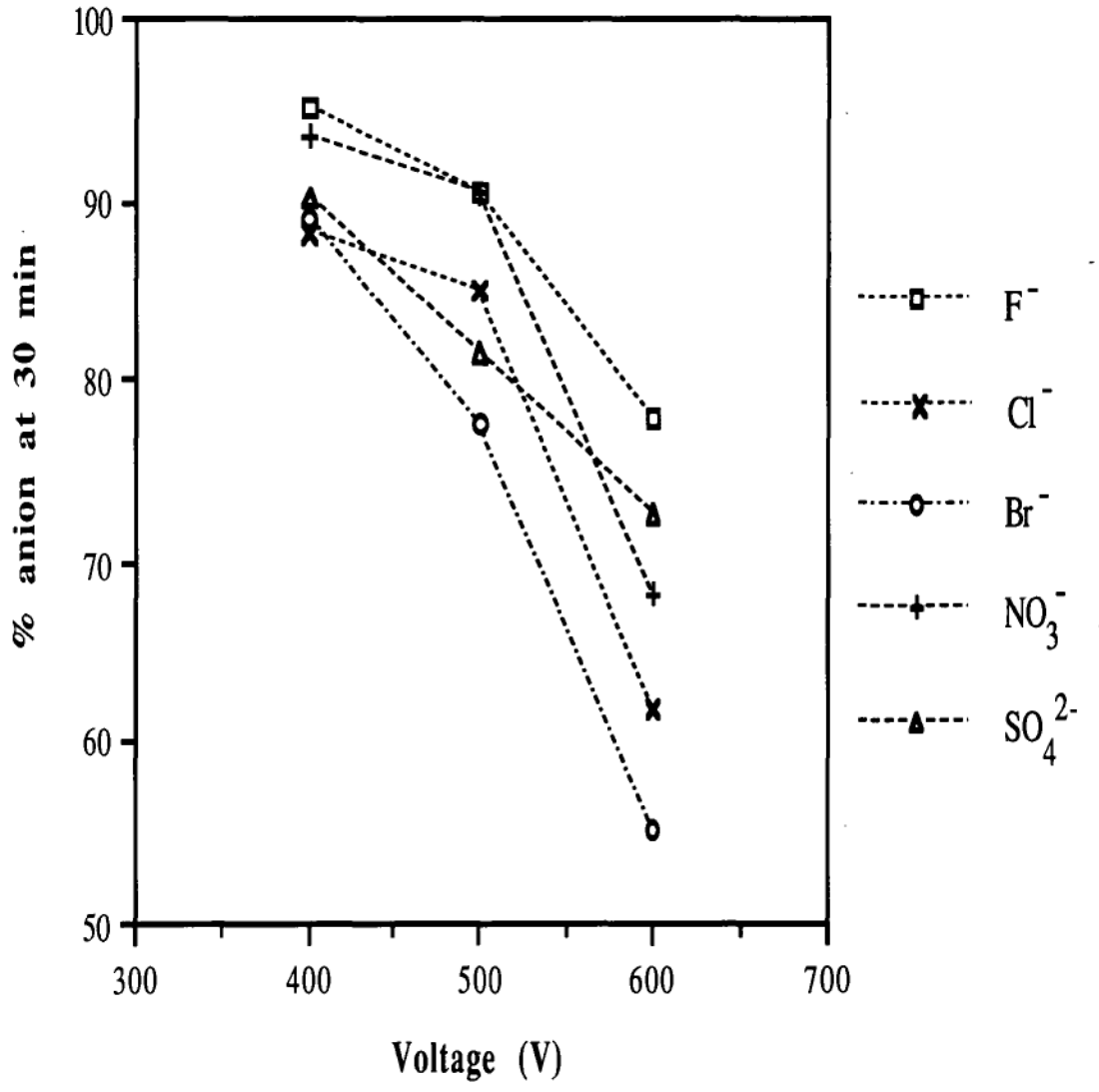


Fig. 5.3 Percentage of anions in the elution compartment at 30 min using different constant potentials.

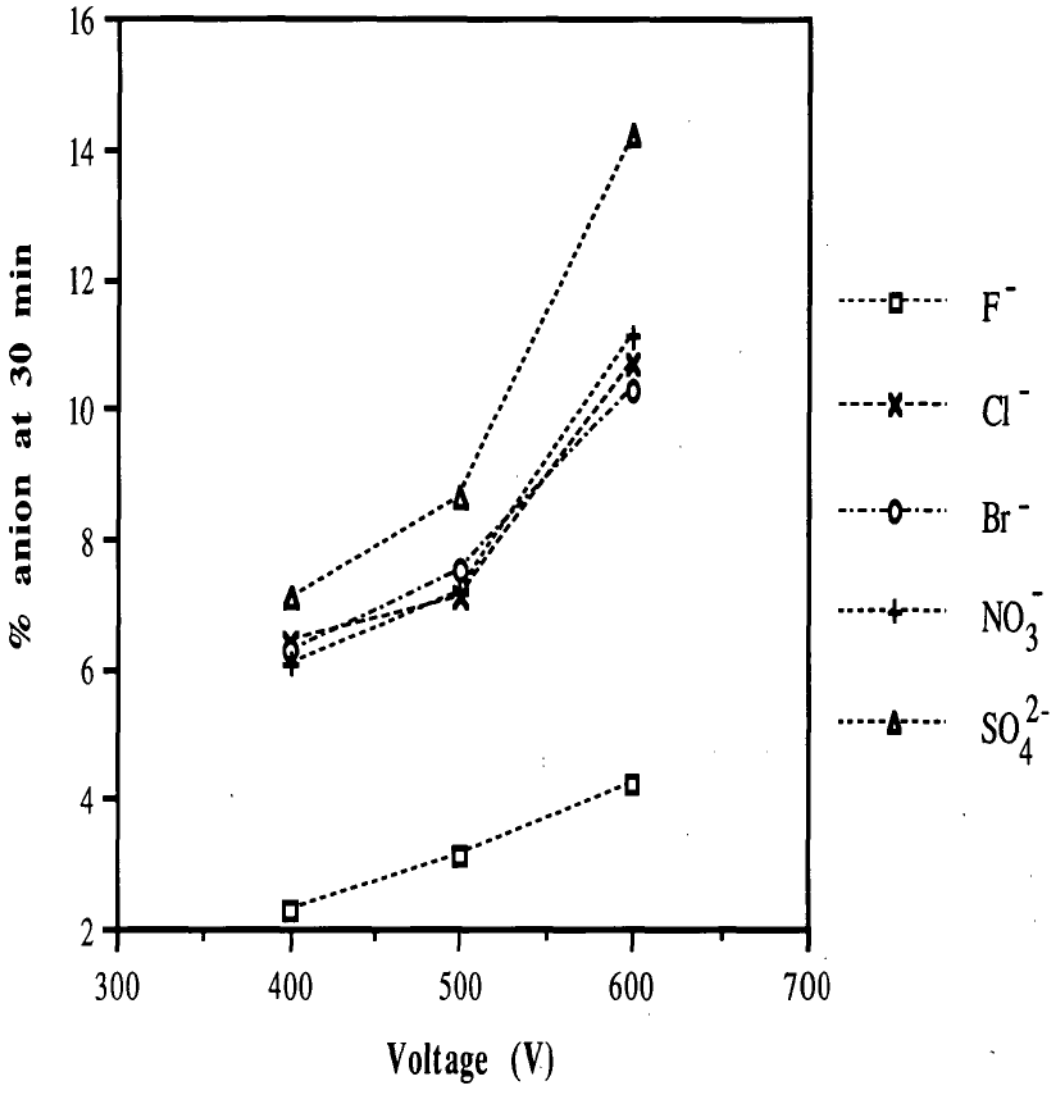


Fig. 5.4 Percentage of anions in the trap compartment at 30 min using different constant potentials.

present in the elution and the trap compartment was always less than 100%. This indicates that during the process the anions passed through the trap compartment and entered the positive electrode (anode) area. It appeared that both of the membranes used in this experiment were incapable of selectively preventing the migration of these low molecular weight anions.

5.3.2 EFFECT OF THE ARRANGEMENT OF THE MEMBRANES

Further examination of the effect of the membrane type on the migration of anions was carried out by applying a constant potential of 500 V to the electromigration of the same sample solution, but with two different arrangements of the membranes as described in the experimental section. The result of using BT1 membranes at positions A, B and C in the "Elutrap" was similar to the results obtained above. This is shown in Fig. 5.5, which illustrates the levels of anions present in the elution compartment, and by Fig. 5.6, which shows the amount of anions in the trap compartment during the electromigration process. However, when BT2 membranes were employed in positions A, B and C the migration rate of all anions was accelerated considerably. This possibly resulted from the larger pore size of the membrane, with the anions being passed directly to the anode area.

The migration pattern obtained using these two arrangements of membranes was the same as that described earlier. This migration order differs from the predicted order of $SO_4^{2-} > Br^- > Cl^- > NO_3^- > F^-$ obtained by consideration the ionic mobilities of the anions. Different migration orders were also obtained by considering the effect of ionic radius and hydrated ionic radius in respect to the pore size of the membrane. The comparison of these migration patterns is shown in Table 5.5 and it can be seen that the migration pattern obtained in this experiment is the same as that obtained by considering the effect of mass/charge ratio of inorganic anions.

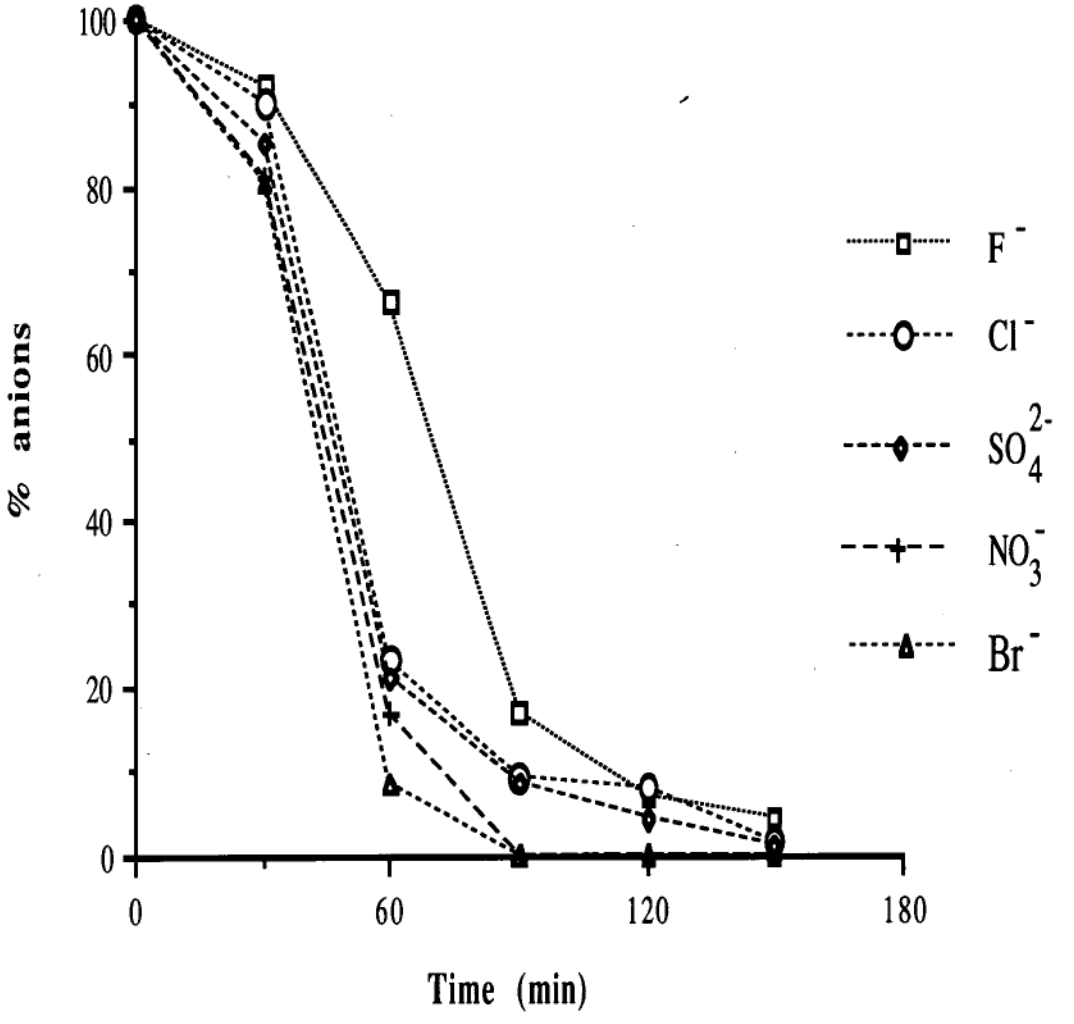


Fig. 5.5 Percentage of anions present in the elution compartment using BT1 membranes in all positions with the applied potential of 500 V.

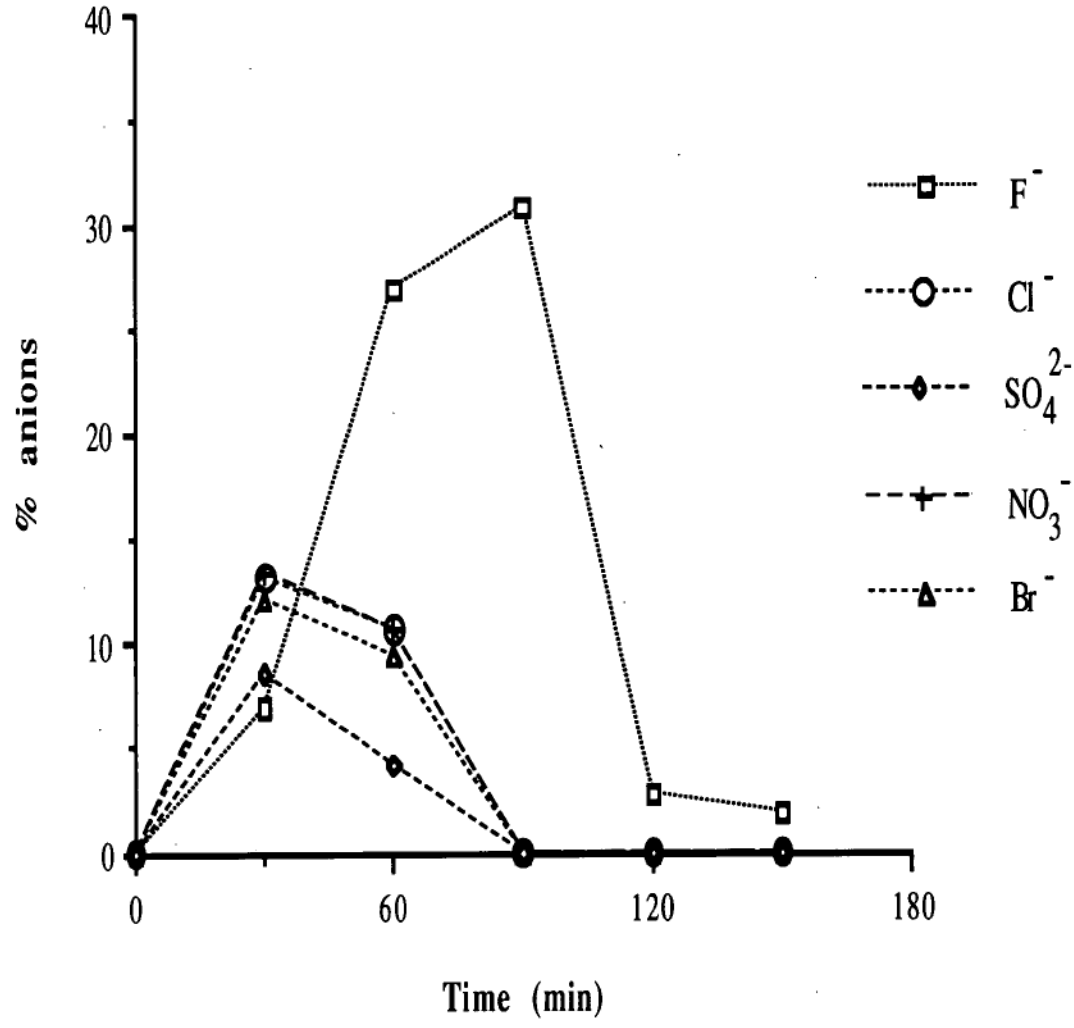


Fig. 5.6 Percentage of anions present in the trap compartment using BT1 membranes in all positions with the applied potential of 500 V.

TABLE 5.5
MIGRATION ORDERS OBTAINED BY CONSIDERING VARIOUS PHYSICAL PROPERTIES OF INORGANIC ANIONS.

Physical properties	Migration pattern
Obtained experimentally	$Br^- > NO_3^- > SO_4^{2-} > Cl^- > F^-$
Charge/mass ratio	$Br^- > NO_3^- > SO_4^{2-} > Cl^- > F^-$
Ionic mobility	$SO_4^{2-} > Br^- > Cl^- > NO_3^- > F^-$
Ionic radius	$F^- > SO_4^{2-} > Cl^- > Br^- = NO_3^-$
Hydrated ionic radius	$Br^- > Cl^- > NO_3^- > F^- > SO_4^{2-}$

It was observed that the migration process of ions in the "Elutrap" apparatus used in this experiment is similar to that occurring in capillary zone electrophoresis, in which the effects of electroosmotic flow are significantly greater than the ionic mobility of the individual ions [8]. In the "Elutrap" apparatus, although the electroosmotic flow is absent, the migration order of the inorganic anions also appeared to be highly influenced by their charge/mass ratios. Anion with the lowest charge/mass ratio (i.e. bromide) was shown to be the earliest anion migrating to the anode, whilst anion with the highest charge/mass ratio (i.e. fluoride) was the last anion to migrate. This indicates that there are possibly some other factors influencing the migration rate of inorganic anions under the experimental condition used in this work. These include the nature of the carrier solution, the pH and temperature of sample solution, and the physical and chemical properties of the membrane. These factors were not examined further as the initial purpose of this study, that is selective removal of anions, was found to be impractical using this electromigration device.

5.4 CONCLUSIONS

This preliminary study has shown that the migration of anions using an "Elutrap" device under the influence of an applied electrical potential is based on the differences in their ionic mobility and size. The charge/mass ratio of the anion exerts a significant effect on the migration rate and this rate increases with the applied potential. The solvated size of the anion also influences the migration rate when this size is close to the pore size of the membrane. Membranes with smaller pore sizes tend to reduce the migration rate. It was shown that both membranes used in this study do not have a suitable pore size to selectivity prevent the inorganic anions from migrating further to the anode. Selective removal of anions, and hence sample enrichment and clean-up in anion IC, was therefore impractical under the experimental conditions described in this study.

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CHAPTER SIX

OFF-LINE ELECTRODIALYSIS FOR CLEAN-UP OF STRONGLY ALKALINE SAMPLES IN ION CHROMATOGRAPHY

6.1 INTRODUCTION

Donnan dialysis involving the transfer of ions of a specified charge through an ion-exchange membrane was shown in Chapter 4 to be a useful method for the neutralization of alkaline samples prior to IC analysis. The limitation of this approach was the fact that the dialysis was diffusion controlled, which restricts the concentration of alkali in the sample to that which can be neutralized in a reasonable time. Further refinement to the active dialysis method can be achieved by coupling electrical fields with membranes. This process is known as electrodialysis and the migration of ions through the ion-exchange membrane is accomplished under the driving force of an electrical field.

Electrodialysis is often performed using a membrane stack in which cation-exchange and anion-exchange membranes are arranged alternatively to form the feed and the concentrate compartments. A typical set-up for electrodialysis, which is exemplified by the desalination of NaCl solution, is shown earlier in Chapter 2 (Fig. 2.4). When a DC electrical potential is applied to the electrodes at the two ends of the stack, the anions migrate toward the anode through the anion-exchange membrane, but are stopped from migrating further by the cation-exchange membrane. Simultaneously, cations migrate toward the cathode through the cation-exchange membrane, but are stopped by the anion-exchange membrane. As a result, ions are depleted from the feed compartment and increased in the concentrate compartment.

The electrodialysis process has been used for many years in industry for water purification, waste water treatment and desalination procedures [1-4]. The first reported analytical application of electrodialysis was for an extraction of aqueous solutions of drugs, such as nicotine, phenobarbital and sulphadiazine, in an off-line procedure involving a dialysis block provided with electrodes and a neutral cellulose membrane [5]. The method was extended to extract a large number of organic acids and bases [6], and basic compounds present in solid matrices [7]. In a later study, ion-exchange membranes were used instead of a cellulose membrane for concentrating Cu(II) and Ni(II) from lake water [8]. The method was also applied to liberate Na(I), K(I) and SCN^- from blood samples [9]. Recently, electrodialysis has been used for on-line sample enrichment in the liquid chromatographic determination of basic and acidic compounds in ground water and surface water [10, 11]. The cell used consisted of a set of spacers and membranes (neutral cellulose acetate membrane and anion-exchange membrane), held between two perspex blocks which contain the electrode compartments.

Apart from the enrichment of charged analytes, electrodialysis has also been reported for the treatment of strongly acidic samples prior to the determination by IC of magnesium(II) and calcium(II) using a dual anion-exchange membrane tube device [12]. In this work, concentric anion-exchange membrane tubes were used to form the sample and electrolyte compartments and migration of anions was induced under conditions of constant current. Cations were prevented from movement between compartments as a result of the permselectivity of the membranes. These authors [12] have also suggested the potential applicability of electrodialysis using the same experimental arrangement for the pre-treatment of alkaline samples prior to analysis using IC. A two-part electrodialysis cell, in which the anode and cathode compartments are separated by a cation-exchange membrane, has been suggested for the treatment of caustic samples containing nitrate and sulfate prior to IC analysis [13]. The process requires 3 h to lower the NaOH concentration in the sample from

19 M to 0.3 M and can only be applied to samples that do not contain analytes that can be oxidized at the anode. Amongst the applications of electrodialysis mentioned above, no systematic study has been reported on the use of this technique for determination of inorganic anions by IC.

In the present work electrodialysis is used for the off-line pretreatment of alkaline solutions prior to their analysis by anion-exchange IC. Such samples are traditionally difficult to analyse by IC because of the severe baseline disturbances generally caused when the sample is injected onto the column. Simple neutralization with acid is not practicable because of the resultant high concentration of the acid anion introduced into the sample. Electrodialysis can be achieved by arranging two sheets of cation-exchange membrane in a stack to form a three-compartment cell comprising compartments for anode, cathode and sample (as shown in Fig 6.1).

The anode compartment contains a hydrogen ion donating medium, the cathode compartment contains a dilute alkaline solution (which acts as a receiver) and the sample compartment is filled with a mixture of inorganic anions in a sodium hydroxide solution. Application of a DC electric field causes cations (especially sodium ions) to move from the sample compartment towards the cathode, and to be replaced by hydrogen ions from the anode compartment. Anions do not move between compartments. The net effect of this process is the neutralization of the alkaline sample solution. During the electrodialysis, water will be oxidized at the anode to produce O_2 and H^+ and will be reduced at the cathode to form H_2 and OH^-. The concentration of OH^- in the cathode compartment therefore increases, whilst the amount of water in the anode compartment decreases at the end of the process.

The stability of the membrane to changes in pH and temperature during electrodialysis is an important factor for the ultimate success of the process, as are

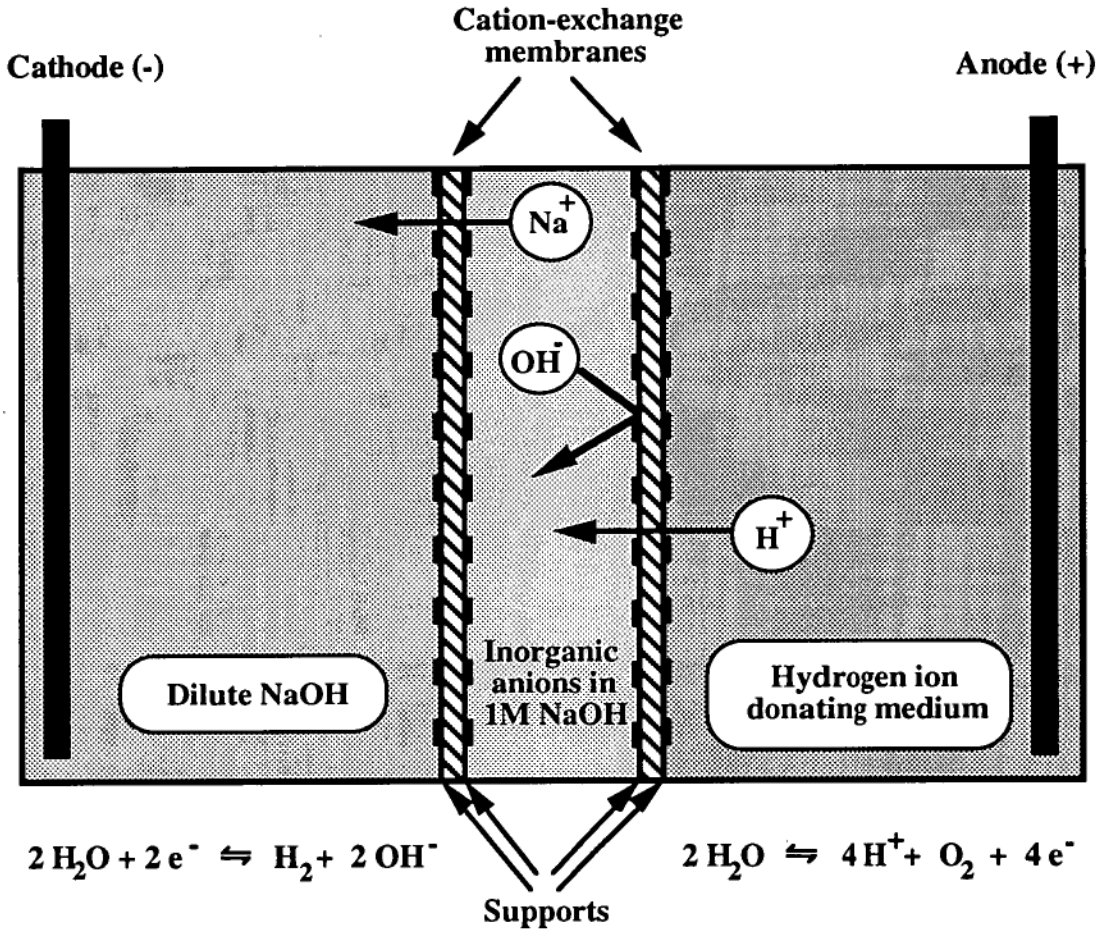

Fig. 6.1 Schematic diagram of the electrodialysis process.

the changes in shape of the membrane which will directly affect the electrodialysis time. Chemical stability and high permselectivity of the membrane also play a significant role in the recovery of inorganic ions present in the sample. In this work, the electrodialysis technique is applied to the neutralization of alkaline samples, with particular attention to the design of a cell suitable to minimize the electrodialysis time and to optimize the electrodialysis conditions.

6.2 EXPERIMENTAL

6.2.1 INSTRUMENTATION

The ion chromatograph consisted of a Millipore-Waters (Milford, MA, USA) model 510 pump, model U6K injector and model 430 conductivity detector, operated in both the suppressed and non-suppressed modes. The column used for non-suppressed mode was a Millipore-Waters IC Pak A anion column, 50 x 4.6 mm ID, packed with polymethacrylate anion-exchange resin. The column used for suppressed IC was a Dionex HPIC AS-4A anion separator with AG-4A guard column, connected to an AMMS membrane suppressor. A Waters Reagent Delivery Module was used to pass the regenerant of 25 mN H_2SO_4 through the suppressor. Sodium ion was determined using a Millipore-Waters IC Pak C cation column, 50 x 4.6 mm ID, packed with styrenedivinylbenzene resin. Chromatography was carried out at room temperature with an eluent flow-rate of 1.2 ml/min. Chromatograms were recorded on a Cole Parmer (Chicago, Illinois, USA) chart recorder and on Millipore-Waters Maxima 820 data station.

6.2.2 ELECTRODIALYSIS DEVICE

The electrodialysis cell used is shown schematically in Fig. 6.1 and in more detail in Fig 6.2. The cell was constructed as a series of cylindrical perspex components held

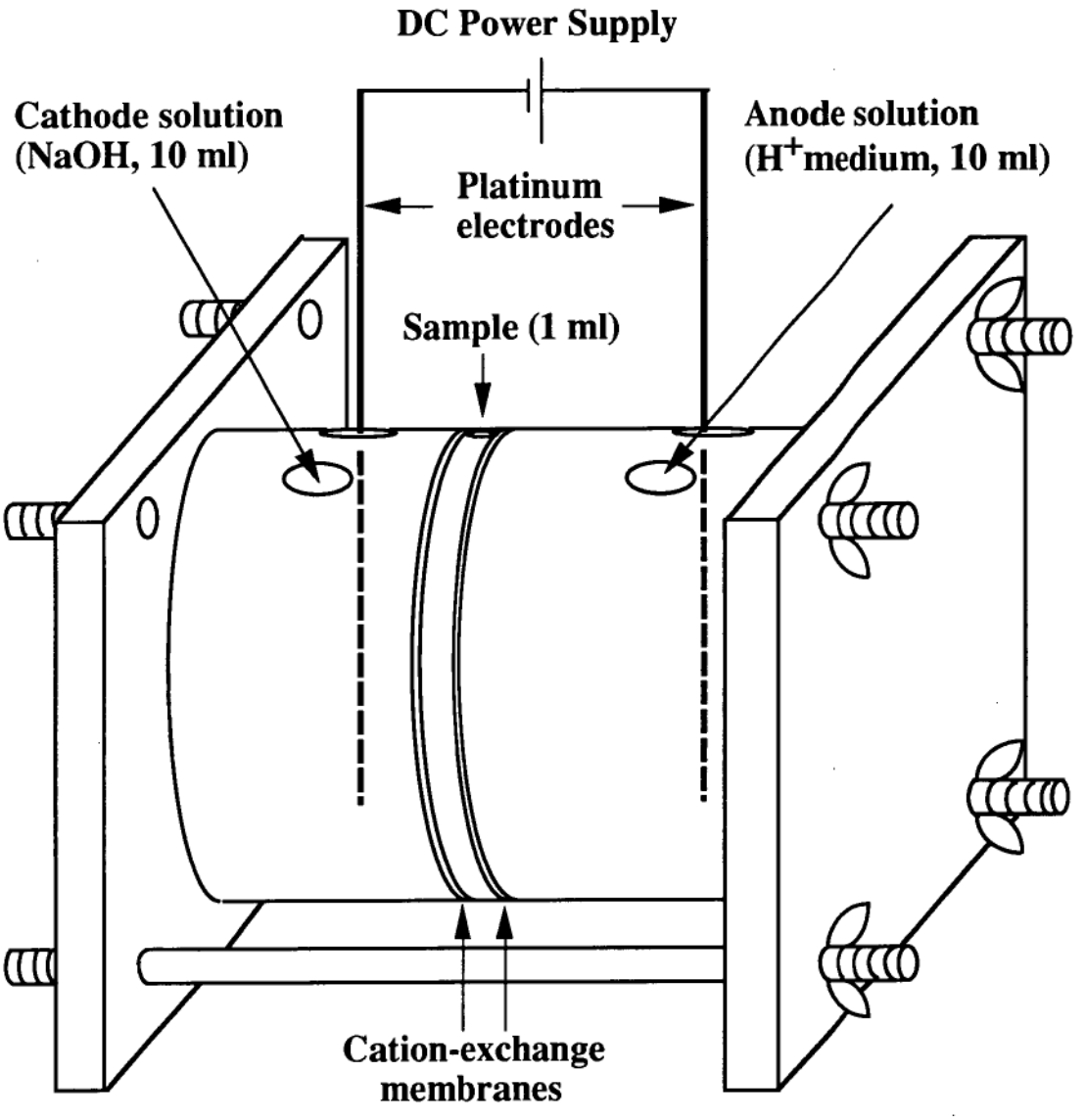

Fig. 6.2 Electrodialysis cell.

together by two plates compressed with longitudinal threaded rods. Electrodes were constructed from platinum wires (60 x 0.25 mm OD), clipped to the cell and connected to the power supply. The cation-exchange membranes were supported on each side with perspex discs (as shown in Fig. 6.1), 0.9 mm in thickness, through which had been drilled closely spaced 3.2 mm diameter holes covering a circular area 28 mm in diameter. Under these conditions, the surface area of the membrane in contact with the sample and electrode solutions was 616 mm^2. The volume of both the anode and cathode compartments was 10 ml, whilst the sample compartment contained 1 ml.

A BioRad (Richmond, CA, USA) microprocessor-controlled electrophoresis power supply (Model 3000 Xi) was used in the fixed potential, fixed current and fixed power modes. When an applied current in excess of 300 mA was required, a GoodWill (Taiwan) laboratory DC power supply (Model GPR-7530D) was used.

6.2.3 REAGENTS

All chemicals used were of analytical reagent grade and the water used in the preparation of standard solutions and eluents was purified on a Millipore (Bedford, MA, USA) Milli-Q water treatment system. Samples and eluents were filtered through a Millipore 0.45 μm membrane filter and degassed in an ultrasonic bath prior to use.

The eluent used for non-suppressed IC analysis of the treated samples contained 1.3 mM sodium tetraborate, 5.8 mM boric acid and 1.4 mM potassium gluconate adjusted to pH 8.5 and made up in water:acetonitrile (88:12,v/v). The eluent for the suppressed system contained 2 mM sodium bicarbonate and 2 mM sodium carbonate. The eluent for sodium determination contained 0.5 M EDTA and 2mM nitric acid.

6.2.3.1 Standard solutions

Standard stock solutions of inorganic anions were prepared by dissolving appropriate amounts of the sodium salts in water. Working solutions of these ions were obtained by diluting the stock solutions to give 1 M sodium hydroxide in the final solution. The concentration of inorganic anions in these solutions are listed below :

Mode of operation	Concentration (µg/ml) of inorganic anions in NaOH solutions
Non-suppressed	F^- (30), Cl^- (30), Br^- (60), NO_3^- (60), SO_4^{2-} (80), HPO_4^{2-} (100)
Suppressed	F^- (3), Cl^- (3), Br^- (6), NO_3^- (6), SO_4^{2-} (8), HPO_4^{2-} (10)

6.2.3.2 Hydrogen ion donating media

Hydrogen ion donating solutions for use in the anode compartment of the electrodialysis cell were prepared using 0.001-0.1 N sulfuric acid (H_2SO_4), methanesulfonic acid (MSA), octanesulfonic acid (OSA), camphorsulfonic acid (CSA) and p-toluenesulfonic acid (TSA). All sulfonic acids were in free acid form and were obtained from Sigma Chemical Company, St. Louis, USA, with the exception of octanesulfonic acid, which was prepared by passing a solution of sodium octanesulfonate through a glass column packed with 100 g BioRad AG 50W-X8 cation-exchange resin (H^+ form, 200-400 mesh). This same cation-exchange resin was also used as hydrogen ion donating medium and prior to its use for this purpose was washed thoroughly with Milli-Q water.

6.2.4 CATION-EXCHANGE MEMBRANES

The cation-exchange membranes used in this work were obtained from Asahi Glass Company, Japan (CMV), Du Pont Company, Delaware, USA (Nafion 324, Nafion 901), Ionics Incorporated, USA (CZL-386, AZL-389), Tokuyama Soda Company, Japan (Neosepta CM-2, CMS, C66-10F, CLE-E), Pall RAI, Inc., USA (Raipore R-5010-M) and Asahi Chemical Company, Japan (K-101).

6.2.5 PROCEDURES

Electrodialysis of samples was carried out with the cathode compartment filled with 0.1 M NaOH solution and the anode compartment filled with a suitable hydrogen ion donating medium. Samples of sodium hydroxide solution containing inorganic anions were introduced into the sample compartment by means of a 500 µl glass microsyringe. The electrical field was then applied to the cell until neutralization of sample occurred, as indicated by a rapid increase of the applied potential or by colour change of a suitable indicator. The neutralized samples were then chromatographed to determine the inorganic anion levels present.

The determination of co-ion concentrations present in a particular membrane was carried out by first soaking the preweighed membrane in Milli-Q water for 24 h to remove any residual ions, after which it was equilibrated in 100 ml of 0.1 M sodium salt solutions (e.g. NaF, NaCl, NaBr, $NaNO_3$, Na_3PO_4, Na_2SO_4) for a further 24 h period and then blotted to dryness. The co-ions present in the membrane were displaced by soaking the membrane for 24 h in 20 ml of 0.3 M potassium chloride for sulfate ion or in 20 ml of 0.2 M potassium sulfate for other anions. The displaced anions were determined by suppressed anion-exchange IC and the displaced sodium ion (which is a measure of the counter ion or exchange capacity of the membrane) was measured by cation-exchange IC. The final concentration of co-ion or counter-

ion was calculated by the following formula :

$$C = \frac{A}{AW \times W}$$

where, C = concentration of co-ion or counter-ion (meq/g)

A = amount of displaced-ion obtained by IC (mg)

AW = equivalent weight of displaced-ion

W = weight of membrane (g)

6.3 RESULTS AND DISCUSSION

6.3.1 SELECTION OF ELECTRODIALYSIS CONDITIONS

Preliminary tests which were carried out by several neutralization processes of 1 M NaOH solution showed that the mechanical stability of the membranes was a major consideration in this work, since distortion of the membrane as a result of the heat generated in the cell was the most common source of failure. Loss of mechanical stability of the membrane produced pronounced buckling and caused an increase in the sample volume and the electrodialysis time. When the membrane was used as an interface in a static cell containing water and 1 M NaOH, with the water fraction being replaced regularly for several days, there was no change in the stability of the membrane. This indicated that distortion of the membrane was caused solely by the heat generated during the electrodialysis process and was not affected by the concentration differential between the sample and the electrode solutions. As part of the development of the cell design, perspex discs (as mentioned in the experimental section) were assembled on both sides of the membranes to provide the mechanical support needed by the membrane. Further use of the electrodialysis cell showed that the perspex disc supports added no significant increase to the electrodialysis time and their use virtually eliminated buckling of the membrane due to heat production.

Since the electrodialysis can be performed by applying the electrical field in three ways, namely constant potential, constant current or constant power, these methods were evaluated with respect to heat evolution in the cell. The constant potential mode was found to give rapid temperature rises, even at the start of the process. For example a constant potential of 100 V caused an almost instant boiling of the sample solution, whilst a constant potential of 30 V applied to a sample of 20 ml of 1 M NaOH caused the temperature of the sample solution to reach 80° C within the first few minutes of the electrodialysis. Lowering the applied potential reduced heat production but neutralization of the sample could not be achieved. For these reasons, electrodialysis at constant potential was not performed further.

Electrodialysis at constant current proved to be suitable in that both the current and voltage (and hence the temperature) could be held fairly constant over most of the electrodialysis, with significant changes occurring only as neutralization was approached and the conductance of the sample decreased. The time required for a particular electrodialysis was found to be inversely proportional to the current density, which in turn was dependent on the surface area of the membrane and the magnitude of the applied current. The dependency of current density on the surface area of the membrane was assessed further by comparing two cells with membrane surface areas of 123 mm^2 and 616 mm^2. Application of a constant current of 150 mA to both cells showed that the time required by the first cell to neutralize the same sample solution was approximately five times longer than the second cell. By applying a constant current of 750 mA to both cells, the electrodialysis time of the bigger cell was five times shorter than the smaller cell. This experiment indicated that the neutralization process was performed most efficiently in the bigger cell. Hence, the cell with a surface area of 616 mm^2 was used for further experiments.

Various currents were tested for the neutralization of sodium hydroxide samples and this study showed that currents in the range 100-200 mA gave effective electrodialysis without excessive heat production under the experimental conditions

used. Similarly, electrodialysis at constant power was also suitable, provided that the applied power did not produce currents outside the working range indicated above. For this reason, the applied power was restricted to about 3 W. In most cases, this applied power produced an approximate current of 150 mA. Further study showed that more aggressive conditions always caused pronounced buckling of the membrane (even when mechanical supports were used) and loss of sample through volatilization.

The differences between the three modes of electrodialysis are illustrated schematically in Fig. 6.3. The changes in potential, current and power with time when fixed potential was applied to the process are shown in Fig 6.3 (a), while Figs 6.3 (b) and (c) show the changes resulting from applying constant current and constant power, respectively. Fig 6.3 (a) shows that the current (mA) and power (W) in the system increased rapidly in response to the increase of the applied potential (V). The temperature of the solutions rose quickly even before the steady state of fixed potential was obtained. In Fig. 6.3 (b), a fixed current was applied and during the process the potential was gradually increased as the conductance of the solutions decreases (and its resistance rises). This also resulted in a slight increase of the power. When the pH of the sample reached neutral, the potential and the power increased rapidly with a slight reduction in the applied current. Rapid heat production occurred at this point. In practice, this heating effect was reduced by limiting the applied current and by terminating the process as soon as the rapid increase of potential was noticed. The result of applying fixed power is given in Fig. 6.3 (c). It can be seen that at the end of the neutralization process there was a slight decrease in the applied power, a moderate increase in the potential and a large decrease in the current. The net effect is a slight increase in the temperature of the solutions, especially as a result of the building up of power inside the cell. The need to reduce temperature rises limits the amount of fixed power that can be applied to the cell.

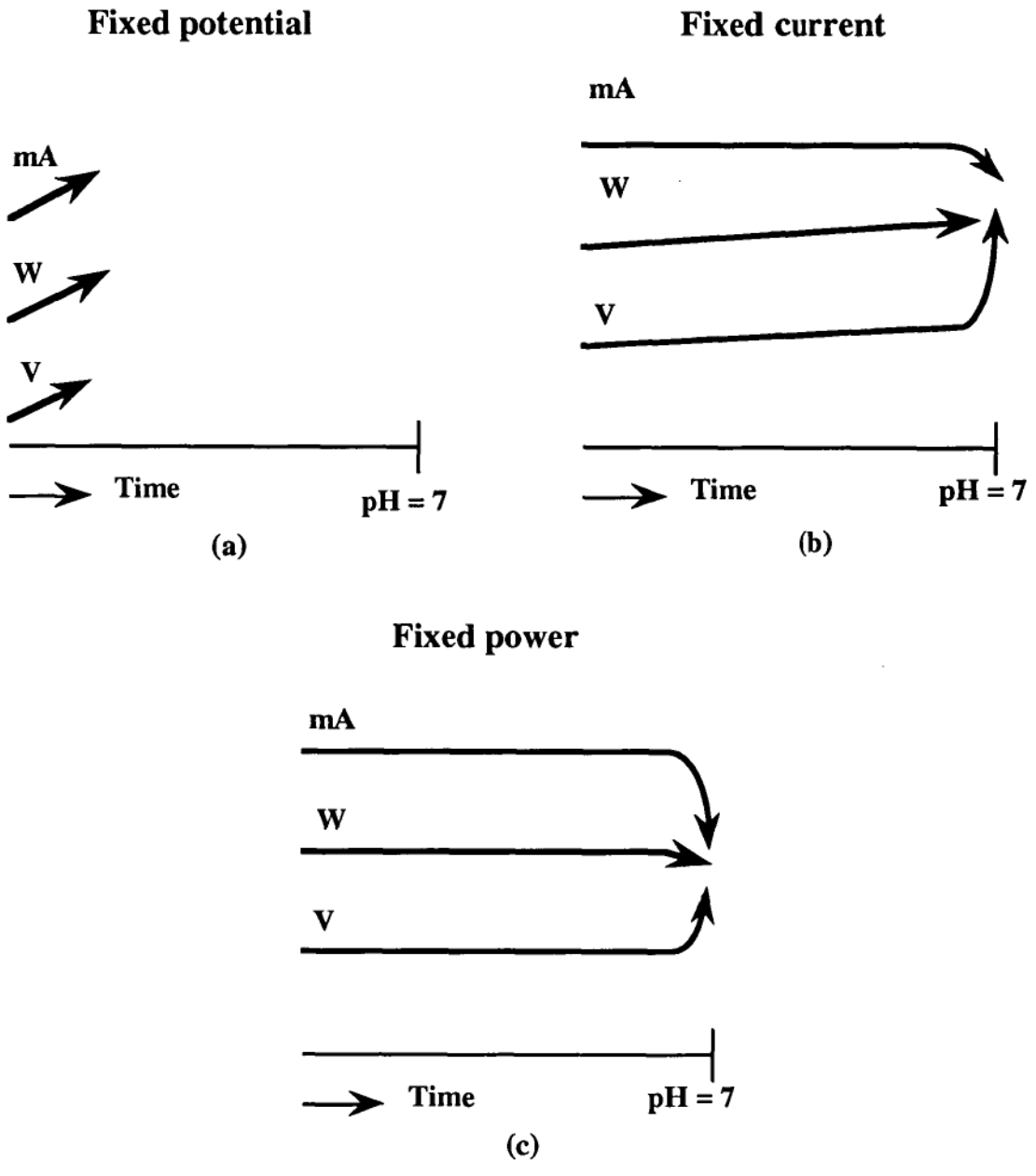

Fig. 6.3 Diagram of changes in the applied electrical fields during electrodialysis.

6.3.2 CELL DESIGN

The cell was designed to optimize the electrodialysis of a sample solution containing up to 1 M sodium hydroxide, since most samples occurring in practice should be dilutable to this level. Varying volumes of sample were dialysed under differing fixed applied currents until neutralization was reached. This point was indicated by either a rapid increase of applied potential or by the change in colour from blue to yellow of bromothymol blue indicator (pKa = 7.0) added to the sample compartment. Tests indicated that there was no penetration of the indicator through the cation-exchange membrane, nor did the presence of the indicator interfere in the analysis of the inorganic anions by non-suppressed or suppressed IC. The cathode compartment of the cell was filled with 10 ml of 0.1 M sodium hydroxide and the anode compartment was filled with 10 ml of 0.1 N sulfuric acid. The membrane used in this experiment was Asahi CMV, a cation-exchange membrane with an ion-exchange capacity of 2.1 meq/g.

Table 6.1 shows the electrodialysis time required under different experimental conditions and indicates that this time was directly proportional to the moles of hydroxide in the sample and inversely proportional to the applied current (note that the membrane area was constant for all experiments). This can be expressed in a simple equation as shown below :

$$T = \frac{C \cdot V}{I}$$

where,

T = time of electrodialysis in seconds.

C = molarity of hydroxide sample.

V = volume of sample in litres.

I = current density in moles/sec (1 A = 10^{-5} moles/sec).

TABLE 6.1
ELECTRODIALYSIS TIMES AT CONSTANT APPLIED CURRENT FOR NEUTRALIZATION OF SAMPLES TO pH 6.

Sample volume (ml)	[NaOH] (M)	Current (mA)	Voltage (V)	Time measured experimentally (min)	Calculated time (min)
20.0	0.1	15	6-50	220	222.2
20.0	0.1	150	10-50	25	22.2
10.0	0.1	15	6-50	115	111.1
10.0	0.1	150	10-50	12	11.1
10.0	1.0	150	10-100	90	111.1
10.0	1.0	450	17-100	30	37.0
10.0	1.0	750	26-100	15.3	22.2
1.0	1.0	150	10-100	11.1	11.1
1.0	1.0	450	18-100	3.9	3.7
1.0	1.0	750	24-100	2.1	2.2

The higher the molarity of the sample, the longer is the electrodialysis time required for the neutralization process. For example, it required 12 min to neutralize 10 ml of 0.1 M NaOH solution with 150 mA of current and 90 min for the neutralization of 10 ml of 1.0 M NaOH solution with the same applied current. On the other hand, a higher current density and a smaller sample volume reduce the electrodialysis time. This can be shown by noting that the electrodialysis times required for the neutralization of 20 ml and 10 ml of 0.1 M NaOH solution were 220 min and 115 min, respectively, at a constant current of 15 mA. By increasing the applied current to 150 mA, the electrodialysis times of both samples were reduced to 25 min and 12 min, respectively.

From Table 6.1, it can be seen that the electrodialysis times obtained experimentally were in close agreement with those calculated using the current density and the known number of moles of hydroxide in the sample. This shows that the cell was performing efficiently. In practical terms, an electrodialysis time of 11 min could be achieved for the neutralization of 1 ml of 1 M NaOH solution by applying a constant current of 150 mA, without the production of excessive heat and resultant distortion of the membrane.

The electrodialysis could be performed on two samples simultaneously by coupling two identical cells in parallel to the same power supply. The total applied current was distributed evenly to both cells and each sample reached the neutralization point at the same time. For example, the electrodialysis time for a single sample containing 1 ml of 1 M NaOH with a current of 150 mA was 11 min, whilst 22 min was required for two parallel cells, each containing 1 ml of the same sample. Increasing the current to 300 mA for the parallel cells reduced the dialysis time to 11 min. This result suggested that the electrodialysis could be carried out in as many parallel cells as necessary provided a suitable total current was applied.

6.3.3 SELECTION OF THE MEMBRANE

The important properties of a range of cation-exchange membranes evaluated for inclusion in the cell are listed in Table 6.2. These membranes must show a high permselectivity towards cations and be able to withstand the heat generated in the cell. All were soaked in water for at least 24 h prior to use, except for Nafion 901 which was soaked in 2% NaOH solution as suggested by the manufacturer.

Preliminary tests showed that the generated heat easily distorted the membranes and the evolution of heat was increased when membranes with higher electrical resistances, such as Neosepta CLE-E and Ionics AZL-389, were employed. However, these membranes were less distorted by the generated heat as they have higher burst strength and are generally thicker than membranes with lower electrical resistance. This deleterious effect was overcome when the membranes were supported with porous perspex discs (as described in the experimental section) and most showed adequate mechanical stability with the exception of the Neosepta CMS, Asahi CMV and Nafion 901 membranes. The Neosepta CM-2 membrane was tested with this arrangement by repeated usage for the neutralization of 1 M NaOH sample solutions and showed minimal distortion even after 20 h use.

The permselectivities of the membranes were assessed by determining the recoveries for a range of inorganic anions initially added to 1 M NaOH before the samples were subjected to electrodialysis until neutralized. The recovery value for the inorganic anions was obtained by comparing the chromatogram of the neutralized sample with a chromatogram of the same concentration of the anion mixture in Milli-Q water. A blank value was determined for the anions present in neutralized 1 M NaOH solution. These anions were usually chloride, sulfate, nitrate and a trace amount of fluoride, which are commonly present as impurities in NaOH solution.

TABLE 6.2
PROPERTIES OF THE COMMERCIAL CATION-EXCHANGE MEMBRANES USED IN THIS STUDY.

Supplier	Type	Electrical resistance (Ω cm^2)	Total cation transport number	Burst strength (kg/cm^2)	Exchange capacity (meq/g)	Thickness (mm)
Asahi Glass	CMV	2.0 - 3.5	>0.92	3 - 5	2.1*	0.13
Du Pont	Nafion 901	2.8	n.a.	n.a.	n.a.	0.45
Du Pont	Nafion 324	4.5	n.a.	n.a.	0.6*	0.32
Ionics	CZL-386	13	n.a.	8	2.7	0.60
Ionics	AZL-389	28	n.a.	27	2.6	1.20
Tokuyama Soda	Neosepta CM-2	2.0 - 3.0	>0.98	3 - 5	2.2*	0.14
Tokuyama Soda	Neosepta CMS	1.5 - 2.5	>0.98	3 - 4	2.4*	0.16
Tokuyama Soda	Neosepta C66-10F	5.0 - 8.0	>0.98	6 - 8	1.7 - 2.2	0.30
Tokuyama Soda	Neosepta CLE-E	15 - 25	>0.98	8 - 10	1.3 - 1.8	1.10
Pall RAI	R-5010-M	4 - 8	0.92	n.a.	n.a.	0.17
Asahi Chemical	K-101	n.a.	n.a.	n.a.	n.a.	0.20

* = value determined experimentally.
n.a. = data not available.

A constant current of 150 mA or a constant power of 3 W were applied to the cell using the membranes listed in Table 6.2. The recovery values for inorganic anions after electrodialysis using the two electrodialysis modes are tabulated in Tables 6.3 and 6.4. Both tables show a similar trend with higher recovery values for fluoride being obtained when the electrodialysis was carried out at constant current. Constant power may have induced a faster diffusion rate of fluoride through the sample compartment which resulted in losses. Some of the thicker membranes (e.g. Ionics AZL-389, Ionics CZL-386, Neosepta CLE-E and Nafion 901) used in this study showed insufficient permselectivity, leading to low recoveries. The results also show that with the exception of fluoride, the Neosepta CM-2 membrane gave recoveries which were close to quantitative.

The preliminary recovery studies of a range of inorganic anions (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}) in the range 30-100 μg/ml using the Asahi CMV membrane, showed that no significant loss of analyte was observed. Further recovery studies with a mixture of lower concentrations (3-10 μg/ml) of the same inorganic anions showed that there was an interference from CO_2 (present as CO_3^{2-}) in the sample solution. During the electrodialysis process, the CO_3^{2-} was protonated to form bicarbonate ion at a level greatly exceeding that of the solute anions to be determined. This bicarbonate ion produced a large peak in the subsequent chromatogram and obscured the presence of other anion peaks, especially fluoride and chloride ions, when the sample was determined by a non-suppressed system. The most simple way to eliminate the bicarbonate peak was to use a suppressed IC system. In this mode, the bicarbonate was protonated in the suppressor and was not detected. The recovery values of inorganic anions using the suppressed IC mode were given in Tables 6.3 and 6.4.

A chromatogram showing the application of the electrodialysis system to the treatment of a 1 M sodium hydroxide solution containing F^-, Cl^-, Br^-, NO_3^-,

TABLE 6.3
PERCENTAGE RECOVERY OF ANIONS (IN THE RANGE OF 3-10 μg/ml) FROM 1 M NaOH SOLUTION AFTER ELECTRODIALYSIS AT 150 mA USING VARIOUS CATION-EXCHANGE MEMBRANES.

The range derived from 5 replicates is shown in parentheses.

Membrane	F^-	Cl^-	Br^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}
Asahi CMV	80.2 (5.0)	62.1 (4.2)	80.0 (5.0)	80.7 (3.5)	80.0 (3.0)	80.2 (2.6)
Nafion 901	59.0 (9.0)	19.1 (1.5)	12.1 (2.4)	15.8 (1.6)	50.3 (2.8)	55.7 (4.7)
Nafion 324	78.9 (4.6)	90.8 (1.5)	75.4 (4.2)	73.3 (0.8)	74.2 (3.1)	75.0 (4.7)
Ionics CZL-386	80.5 (3.5)	53.0 (2.6)	57.9 (2.3)	72.0 (2.4)	75.7 (2.0)	77.5 (1.0)
Ionics AZL-389	32.7 (1.9)	36.3 (1.0)	45.1 (0.3)	60.8 (1.5)	57.4 (1.6)	54.0 (1.7)
Neosepta CM-2	21.9 (3.2)	98.4 (3.6)	92.5 (1.0)	94.8 (1.8)	95.6 (2.2)	91.5 (3.0)
Neosepta CMS	82.4 (4.3)	72.1 (3.0)	81.1 (4.5)	83.4 (2.3)	81.3 (1.2)	73.7 (1.5)
Neosepta C66-10F	50.8 (5.5)	60.5 (3.8)	89.2 (3.5)	89.2 (4.3)	92.8 (2.8)	96.0 (3.0)
Neosepta CLE-E	53.0 (3.0)	57.5 (4.0)	76.6 (4.5)	78.1 (3.4)	80.0 (4.2)	84.6 (5.2)

TABLE 6.4
PERCENTAGE RECOVERY OF ANIONS (IN THE RANGE OF 3 -10 µg/ml) FROM 1 M NaOH SOLUTION AFTER ELECTRODIALYSIS AT 3 W USING VARIOUS CATION-EXCHANGE MEMBRANES.

The range from 5 replicates is shown in parentheses.

Membrane	F^-	Cl^-	Br^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}
Neosepta CM-2	4.4 (2.1)	96.1 (4.2)	94.1 (4.4)	97.3 (3.2)	98.5 (1.4)	89.5 (5.4)
Asahi CMV	30.0 (4.3)	87.2 (6.5)	85.7 (6.9)	87.4 (6.2)	85.6 (3.6)	66.5 (7.8)
Asahi K-101	55.0 (5.0)	79.4 (8.1)	75.6 (3.8)	80.9 (3.4)	80.6 (4.2)	80.7 (6.3)
Neosepta CMS	9.2 (3.6)	86.8 (8.7)	88.9 (7.3)	87.5 (6.3)	83.6 (3.6)	78.7 (2.4)
Raipore R-5010-M	19.4 (6.0)	78.8 (2.5)	83.2 (4.3)	83.8 (4.8)	82.8 (2.6)	80.3 (6.8)
Nafion 324	35.0 (2.0)	73.0 (5.2)	86.8 (4.1)	90.4 (3.5)	85.3 (3.6)	76.8 (3.8)
Nafion 901	33.3 (4.5)	69.2 (7.0)	83.6 (6.5)	91.2 (5.6)	83.2 (4.2)	76.6 (3.4)

HPO_4^{2-} and SO_4^{2-} in the concentration range 3-10 μg/ml is given in Fig. 6.4. Fig. 6.4 (a) shows the treated sample, whilst Fig. 6.4 (b) shows a chromatogram for the same initial concentrations of anions in Milli-Q water. The two chromatograms are virtually identical, except for the low recovery of fluoride in the treated sample. By contrast, the chromatogram obtained for the original sample before electrodialysis showed no solute peaks whatsoever, but rather a single, large solvent peak which obscured the entire chromatogram.

Recovery data of the type determined here are governed by the degree to which the anionic solutes (i.e. solutes having the same charge as the membrane, or "co-ions") can diffuse into the negatively charged membrane. This diffusion for any specified co-ion can be measured by equilibrating the membrane with a solution of that anion (generally by soaking for 24 h), drying the membrane by blotting and then displacing any co-ion from the membrane using a relatively concentrated solution of another anion. For example, the diffusion of fluoride into the membrane could be measured by first soaking the membrane in 0.1 M sodium fluoride (pH = 5.5) and then displacing with 0.2 M potassium sulfate. The displaced fluoride can be measured by IC, as can the concentration of sodium displaced, which is a measure of the ion-exchange capacity of the membrane.

In practice, potassium chloride was used as the displacement solution when sulfate was determined as the co-ion. This was merely due to the chromatographic behaviour of chloride which has an earlier retention time than sulfate. The baseline of the chromatogram can be restored after the large response for chloride, and an undistorted sulfate peak can then be produced. However, potassium sulfate solution was used as the displacement solution for other co-ions, since the retention times of these species are shorter than for sulfate and they can therefore be quantitated in the presence of a high response for sulfate. Table 6.5 shows the co-ion concentrations found in some of the membranes shown earlier to have promise for electrodialysis.

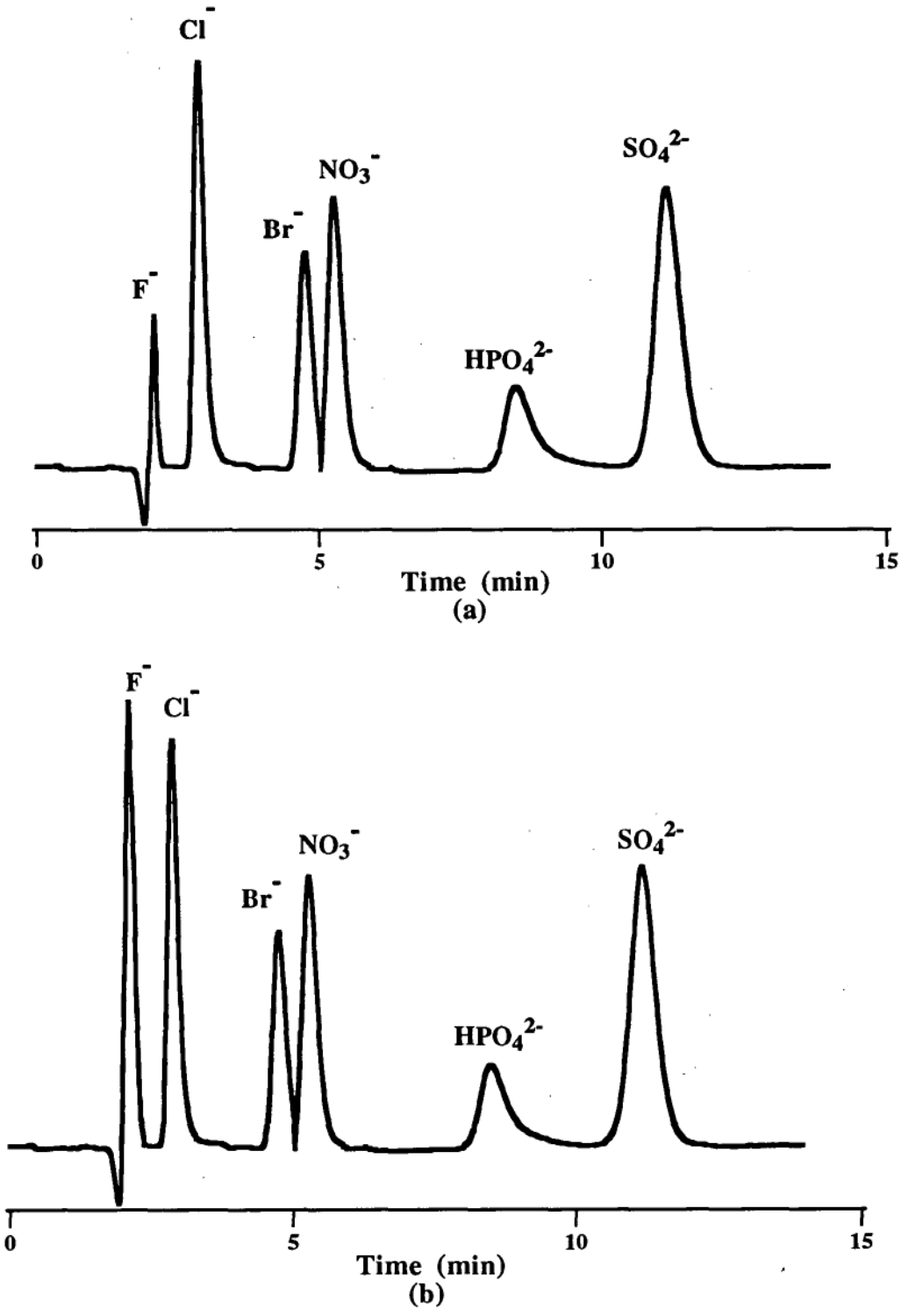

Fig. 6.4 Chromatograms of inorganic anions (3-10 µg/ml) in (a) 1 M NaOH after electrodialytic treatment and (b) Milli-Q water. Injection volume : 10 µl. Eluent : 2.0 mM Na_2CO_3 - 2.0 mM $NaHCO_3$. Column : Dionex HPIC-AS4A with AG4A Guard Column and AMMS Suppressor.

TABLE 6.5
CO-ION CONCENTRATIONS FOR DIFFERENT CATION-EXCHANGE MEMBRANES.

	Co-ion concentration (meq/g)			
Anion	Neosepta CM-2	Neosepta CMS	Asahi CMV	Nafion 324
F^-	0.13	0.07	0.05	0.02
Cl^-	0.002	0.003	0.007	0.002
Br^-	0.001	0.001	0.008	0.006
NO_3^-	0.001	0.002	0.009	0.009
SO_4^{2-}	0.001	0.003	0.009	0.004
HPO_4^{2-}	0.022	0.022	0.020	0.025

From Table 6.5, it can be seen that the concentrations vary significantly, illustrating that there are substantial differences in the permselectivities of the membranes. With the exception of fluoride, the overall co-ion concentration of Neosepta CM-2 membrane is the lowest amongst these membranes.

Comparison of Tables 6.3, 6.4 and 6.5 highlights the fact that an elevated co-ion concentration for a particular membrane is reflected by a reduced recovery for that ion after electrodialysis. For example, the Neosepta CM-2 membrane gave the highest concentration of fluoride and the lowest recovery for this ion. On the other hand, a higher recovery of fluoride was obtained by using the Nafion 324 membrane which gave the lowest co-ion concentration of fluoride. Despite this, the CM-2 membrane gave the best overall performance and, with some supplementation by the Asahi CMV membrane, was used in further studies.

The consistently low recoveries obtained for fluoride for all membranes merits comment. The most plausible explanation for the low recoveries is that partial protonation leads to the formation of neutral hydrofluoric acid which can then diffuse through the membrane. The electrodialysis was terminated when the sample solution reached pH 6, so it would not be expected that there would be any significant formation of hydrofluoric acid (pKa = 3.17). However, it must be remembered that the pH inside the membrane is likely to be much lower than that existing in the bulk external solution because under the Donnan effect, there is an accumulation of cationic species inside the membrane compared to the bulk solution. This accumulation ratio is often very high [14], so that protonation of fluoride is therefore quite probable. Under these conditions, there was possibly a mixture of fluoride ion and protonated fluoride in the measurement of the co-ion concentration. In order to prove this hypothesis, a further determination of fluoride co-ion was carried out with a variation in the pH of the soaking solutions. These soaking solutions were 0.1 M sodium fluoride which were preadjusted to pH 7 and 10 with dropwise addition of

NaOH solution. The fluoride co-ions present in the membranes were displaced by soaking them in potassium sulfate solutions for 24 h and for 6 days. Variation in the displacement time was to determine the efficiency of the displacement process. The results are tabulated in Table 6.6.

From the table, it can be seen that the same values of fluoride concentrations were obtained with soaking solutions of pH 7 and 10, but these results are lower than for pH 5.5. This indicated that the protonation of fluoride occurred to a lesser extent when the pH of external solution was 7 or 10 than at pH 5.5. These results suggest that the consistently low recovery value of fluoride described earlier were caused by the diffusion of hydrofluoric acid formed at the terminating point of the dialysis. The table also shows that the values of fluoride for some membranes measured after they were soaked in the displacement solution for 6 days were higher than those obtained after 24 h. This was caused mainly by some evaporation of the solution during that period of time. The result also indicates that the ions are efficiently displaced after 24 h.

TABLE 6.6
FLUORIDE CO-ION CONCENTRATIONS FOR DIFFERENT CATION-EXCHANGE MEMBRANES SOAKED WITH NaF SOLUTIONS AT pH 7*.

	Fluoride co-ion concentration (meq/g)			
Soaking time	Neosepta CM-2	Neosepta CMS	Asahi CMV	Nafion 324
24 h	0.05	0.02	0.02	0.01
6 days	0.05	0.03	0.03	0.01

* = The same set of data was obtained when the membranes were soaked with NaF solutions at pH 10.

The results reported above indicate the importance of the final pH of the electrodialysis process in preventing the formation of hydrofluoric acid which is eventually lost from the sample compartment. During the electrodialysis process the final pH of the sample solution was approximately 6 and this was chosen to obtain suitable resolution in the ion chromatogram and to reduce the deleterious effect of high sample pH on the ion-exchange column. The co-ion determination results suggested that a higher final pH of the sample solution would possibly avoid the formation of hydrofluoric acid and consequently increase the recovery value of fluoride. Further electrodialysis of fluoride solutions using the CM-2 membrane were then carried out and an average recovery of 53% was obtained when the process was terminated at pH 10. However, this improved recovery value was still low and indicates that electrodialysis of solutions containing fluoride, using the electrodialysis conditions employed in this experiment, is not practicable.

In a similar manner to fluoride, the determination of nitrite co-ion concentration was carried out and the results were tabulated in Table 6.7.

TABLE 6.7
NITRITE CO-ION CONCENTRATIONS FOR DIFFERENT CATION-EXCHANGE MEMBRANES AFTER 24 H SOAKING IN $NaNO_2$ SOLUTION.

	Nitrite co-ion concentration (meq/g)			
pH of $NaNO_2$	Neosepta CM-2	Neosepta CMS	Asahi CMV	Nafion 324
6	0.0031	0.0033	0.0063	0.0011
8 and 10	0.0019	0.0020	0.0026	0.0006

It was noted that the nitrite co-ion concentrations showed the same trend as fluoride, with a higher value being obtained when the soaking solution was at pH 6. The amount of nitrite co-ion in the membrane was the same for soaking solutions of pH 8 and 10. Losses of nitrite can be predicted during the electrodialysis process due to the formation of nitrous acid (pKa = 3.14).

Further recovery studies in the electrodialysis of alkaline nitrite solutions with the Neosepta CM-2 membrane were therefore carried out and variations in the final pH of the process were studied. Average recoveries of 20.9% and 26.5% were obtained when the process was terminated at a pH of 6 and 9, respectively. These figures show that the higher pH of the sample reduces the formation of nitrous acid and also the diffusion of this species from the sample compartment. A further complication observed in this particular experiment was the appearance of a small nitrate peak in the final chromatogram (equivalent to 5.4% of the original nitrite), presumably from oxidation of nitrite.

These studies on fluoride and nitrite indicate the importance of the final pH of the sample solution after the electrodialysis process. When the final pH is lower than 7, weak acid anions, such as fluoride and nitrite, will be protonated to some extent, as their pKa values (3.17 and 3.14 respectively) are approached by the pH inside the membrane. Anions of strong acids, such as chloride, bromide, nitrate and sulfate, have much lower pKa values and they remain in their ionic form when the electrodialysis is terminated. Thus, the diffusion of these anions from the sample compartment is avoided. Phosphate, with a pKa_1 value of 2.1 did not seem to be affected by this phenomenon since more than 90% was usually recovered. The phosphate is most likely to be present in the form of HPO_4^{2-} at the end of the electrodialysis process.

The exchange capacities of the cation-exchange membranes used in this study were determined by measuring counter-ion concentrations in conjunction with the above determination of the co-ions. The counter-ion of the membrane was converted to sodium ion by soaking the membrane in a sodium salt solution, and this was then displaced by potassium ion as described in the experimental section. The results for the determination of the displaced sodium by cation-exchange IC are shown in Table 6.8. From the table, it can be seen that the exchange capacities of the membranes obtained experimentally were similar to the values given by the manufacturer, thereby demonstrating the efficacy of the determination procedure.

TABLE 6.8
EXCHANGE CAPACITIES OF DIFFERENT CATION-EXCHANGE MEMBRANES, DETERMINED AS THE CONCENTRATION OF SODIUM ION TAKEN UP BY THE MEMBRANE.

	Exchange capacity (meq/g)	
Membrane	Given by the manufacturer	Determined experimentally
Neosepta CM-2	1.8 - 2.2	2.2
Neosepta CMS	2.0 - 2.5	2.4
Asahi CMV	n.a.	2.1
Nafion 324	n.a.	0.6

n.a. = data not available

6.3.4 SELECTION OF HYDROGEN ION DONATING MEDIUM

After design of a suitable cell and selection of the optimal electrodialysis mode and membrane type, the next step was to determine the best composition of the hydrogen ion donating medium used to fill the anode compartment. Important factors to be considered in the choice of the hydrogen ion donating medium are the degree of sample contamination resulting from penetration of the acid anion through the cation-exchange membrane, and the effect on performance parameters such as the time of dialysis and the amount of heat produced. As in the previous studies on treatment of alkaline samples using Donnan dialysis, a range of aliphatic and aromatic sulfonic acids was compared with sulfuric acid and with slurries of cation-exchange resin in acid solution.

All of the hydrogen ion donating media gave similar performances (with the CMV membrane) in terms of electrodialysis time and heat production, but significant differences were observed in the degree of incursion of acid anion into the sample. Table 6.9 shows the penetration of acid anions from solutions of hydrogen ion donating media into the sample after electrodialysis at different fixed currents. The concentration of the acid anions found in the sample solution after dialysis is expressed as a percentage of the initial concentration of this anion in the solution of hydrogen ion donating medium.

From the table, it can be seen that the degree of incursion generally increased with the concentration of the hydrogen ion donating solution and with the applied current. Surprisingly, sulfate showed less penetration than the larger sulfonate anions. Solutions of 0.1 M Millipore-Waters SPR-H^+ reagent diluted in 5 mM acid solution were also used but all showed incursion of acid anion, and in most cases heat was generated during the process. This is possibly attributable to the more conductive characteristics of this reagent.

TABLE 6.9

PENETRATION OF ANION FROM THE HYDROGEN ION DONATING MEDIUM (ANODE COMPARTMENT) INTO THE SAMPLE, EXPRESSED AS A PERCENTAGE OF THAT INITIALLY PRESENT IN THE ANODE COMPARTMENT.

The Asahi CMV membrane was used.

H^+-donating medium	0.1 N			0.05 N		
	150 mA	300 mA	450 mA	150 mA	300 mA	450 mA
H_2SO_4	0.06	0.06	0.09	0.03	0.03	0.04
MSA	2.7	4.3	4.6	2.1	2.3	2.5
TSA	2.7	3.6	8.6	0.1	0.2	0.2
CSA	1.0	1.7	2.5	0.3	0.5	0.5
OSA	1.7	2.5	6.7	0.05	0.1	0.1

Incursion of acid anion into the sample was also noticed when the hydrogen ion donating media were used at a fixed current of 150 mA with Nafion 324 and Ionics CZL-386 membranes. The results obtained are given in Table 6.10, which shows that less incursion was obtained with the larger sulfonate anions. The degree of acid incursion on these two thicker membranes appeared to be less than of the Asahi CMV membrane. However, these membranes do not show the required degree of permselectivity and were not tested further.

One possible means to reduce penetration of the acid anion is to use a cation-exchange resin in the hydrogen form as the hydrogen ion donating medium [15]. This approach has been utilized successfully in earlier studies on Donnan dialysis. However, these studies also showed that resin beads can act as effective hydrogen ion donating media only when they are used as a slurry with a suitable acid solution. The interstitial acid solution is necessary for site-to-site transport of hydrogen ions from the bulk slurry to the membrane surface. Some penetration of the anion of the slurrying acid is therefore possible, but this can be minimized by keeping the concentration of this acid as low as practicable.

Studies showed that BioRad AG 50W-X8 (H^+ form, 200-400 mesh) cation-exchange resin slurried in a 2:1 (w/v) ratio with 1 mM toluenesulfonic acid, octanesulfonic acid or camphorsulfonic acid acted as a suitable hydrogen ion donating medium, without any measurable penetration of the acid anion into the sample solution during electrodialysis. Electrodialysis times were increased marginally (approximately 5-10%) over those obtained with the solutions of hydrogen ion donating media of higher concentration used for Table 6.9, but this was considered to be a minor drawback. 1mM octanesulfonic acid was therefore used as the slurrying solvent for the cation-exchange resin.

TABLE 6.10
PENETRATION OF ANION FROM THE HYDROGEN ION DONATING MEDIUM (ANODE COMPARTMENT) INTO THE SAMPLE, EXPRESSED AS A PERCENTAGE OF THAT INITIALLY PRESENT IN THE ANODE COMPARTMENT.

H^+-donating medium	0.05 N	
	Nafion 324	Ionics CZL-386
H_2SO_4	14.3	0.06
MSA	1.9	0.3
TSA	< 0.01	0.02
CSA	< 0.01	< 0.01
OSA	< 0.01	< 0.01

6.4 CONCLUSIONS

Provided correct attention is paid to the design of the cell and the manner in which the current (or power) is applied, electrodialysis can be used for the rapid neutralization of strongly alkaline samples as a clean-up step for IC. A 1 ml sample of 1 M sodium hydroxide could be neutralized in about 11 min, without loss of strong acid anions present in trace amounts in the sample. Weak acid anions, such as fluoride and nitrite, gave poor recoveries, probably due to protonation reactions occurring within the membrane leading to the formation of neutral species which could diffuse from the sample compartment. Electrodialysis under the conditions used in this study is therefore not recommended for these ions. Multiple samples can be treated simultaneously without extending the electrodialysis time by using several cells arranged in parallel.

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CHAPTER SEVEN

ON-LINE PRETREATMENT OF ALKALINE SAMPLES USING A FLOW-THROUGH ELECTRODIALYSIS DEVICE

7.1 INTRODUCTION

In Chapter 6, an electrodialysis technique was used to successfully neutralize moderately concentrated sodium hydroxide solutions containing trace levels of inorganic anions prior to IC analysis. The process was carried out off-line using a three-compartment electrodialysis cell formed by arranging two sheets of cation-exchange membranes in a stack. The factors affecting the neutralization process were then elucidated. The cell employed in this study was difficult to use as samples need to be introduced by means of a glass syringe. In addition, the electrodialysis was rather slow. For these reasons, a further investigation was carried out to improve the speed and efficiency of the electrodialysis process.

In the present work, some modifications to the off-line electrodialysis cell were made to produce a flow-through electrodialysis cell which would permit the sample to flow during the neutralization process. The cell was connected to a switching valve fitted with a sample loop so that direct injection of the sample onto the ion chromatograph could be accomplished after sample treatment. Variations of the shape of the sample chamber, the size of the electrodes and the nature of the cation-exchange membrane were examined in order to optimize the flow-through cell design and to minimize the heat generated inside the cell. In addition, the utility of the procedure for use with samples containing high levels of carbonate or borate was studied. Finally, the

method was applied to the determination of inorganic anions in samples prepared by hydroxide fusion. The samples chosen were those of importance in monitoring the environmental impacts of an aluminium smelter [1]. Aluminium is produced by electrolysis of alumina (Al_2O_3) at about 980^0 C in a melt consisting mainly of cryolite (Na_3AlF_6), a compound which contains fluorine. Gaseous and particulate fluorine compounds may evaporate from this melt and if emitted to the atmosphere may cause undesirable effects on the environment in the close vicinity. Pollutants other than fluorine compounds, e.g. tar aerosols and oxides of sulfur are also emitted, but generally are considered less important. Samples from an aluminium refinery environment (such as air, water, soil and vegetation) must therefore be analysed, especially for their fluoride content, considering the toxicity of this anion to both flora and fauna. The result of the determination of inorganic anions present in the samples by IC were compared with other determination procedures including colorimetry and capillary electrophoresis (CE) method.

7.2 EXPERIMENTAL

7.2.1 INSTRUMENTATION

The ion chromatograph consisted of a Millipore-Waters (Milford, MA, USA) model 510 pump, model U6K injector and model 430 conductivity detector, operated in both the suppressed and non-suppressed modes. The column used for the suppressed mode was a Dionex HPIC AS-4A anion separator with AG-4A guard column, connected to an AMMS membrane suppressor. A Waters Reagent Delivery Module was used to pass the regenerant of 25 mN H_2SO_4 through the suppressor. The column used for the non-suppressed mode was a Millipore-Waters IC Pak HR anion-exchange column. Sodium ion was determined using a Millipore-Waters IC Pak C cation column, 50 x 4.6 mm ID, packed with styrenedivinylbenzene resin. Chromatography was carried out at room temperature with an eluent flow-rate of

1.2 ml/min and chromatograms were recorded on a Millipore-Waters (Milford, MA, USA) Maxima 820 data station.

The CE instrument used was a Waters (Milford, MA, USA) Quanta 4000 with a Waters Maxima 820 data station. The determinations of anions present in dust samples were carried out using conventional fused-silica capillaries obtained from Waters. Data were collected at 20 points per second and detection was carried out using indirect UV at 254 nm.

7.2.2 FLOW-THROUGH ELECTRODIALYSIS DEVICE

The flow-through electrodialysis cell was developed from the two-membrane static electrodialysis cell described in Chapter 6 and was constructed as a series of perspex blocks held together with longitudinal screws to form a three-compartment cell separated by cation-exchange membranes, as depicted in Fig. 7.1.

The sample chamber was designed to allow the sample to flow during the electrodialysis process. Electrodes were constructed from stainless steel plates (60 x 25 x 0.7 mm), inserted into the electrode compartments and connected to the power supply. The membranes were supported with a perspex sheet attached to each electrode solution compartment, through which had been drilled numerous closely spaced holes 2 mm in diameter. The volume of both the anode and cathode compartments was 15 ml, whilst the sample compartment contained 300 µl. A BioRad (Richmond, CA, USA) microprocessor-controlled electrophoresis power supply (Model 3000 Xi) was used in the fixed power and fixed current modes.

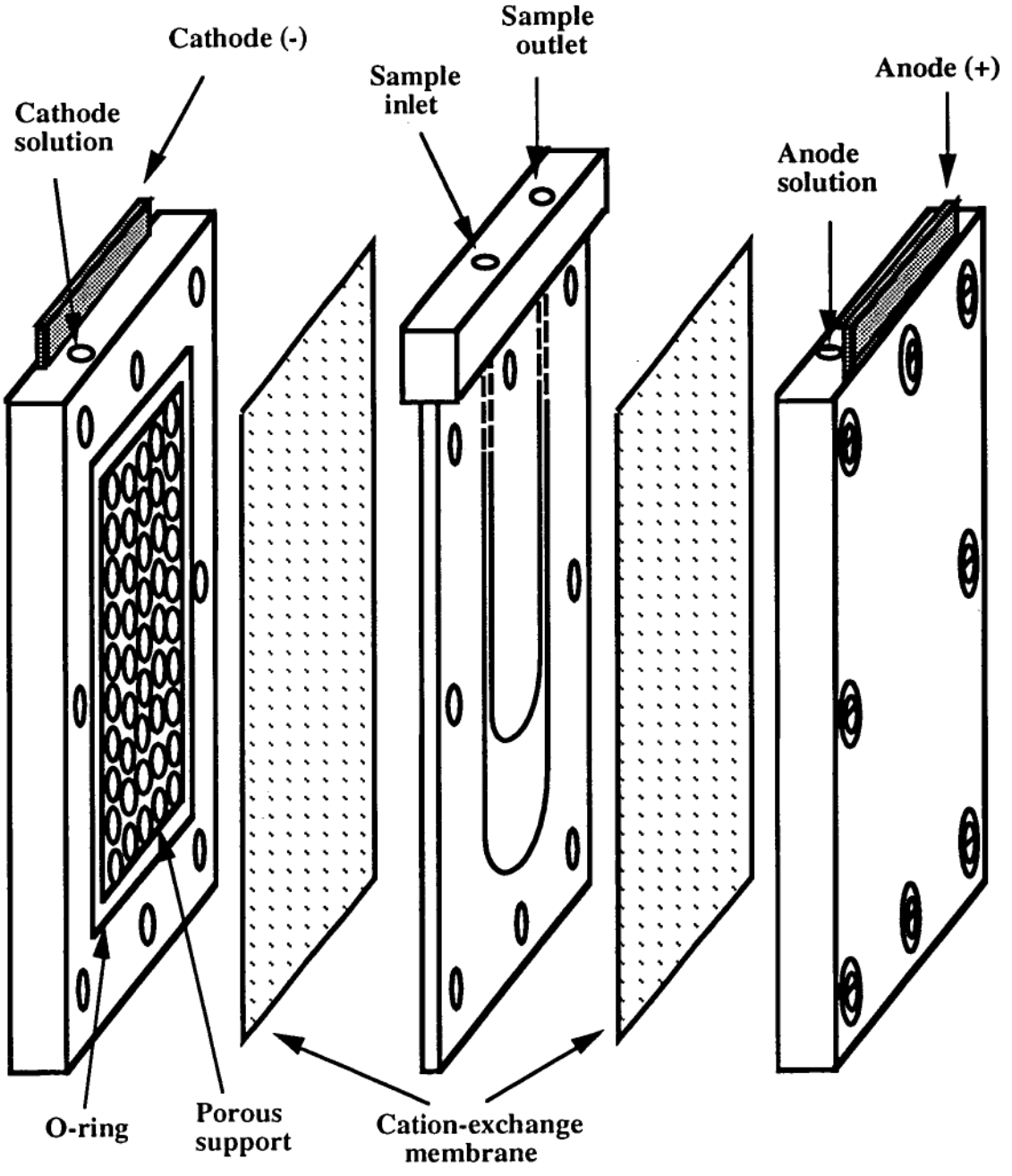

Fig. 7.1 Flow-through electrodialysis cell.

7.2.3 REAGENTS

All chemicals used were of analytical reagent grade and the water employed for the preparation of standard solutions and eluents was purified on a Millipore (Bedford, MA, USA) Milli-Q water treatment system. Samples and eluents were filtered through a Millipore 0.45 μm membrane filter and degassed in an ultrasonic bath prior to use. The eluent used for the suppressed IC mode contained 2 mM sodium bicarbonate and 2 mM sodium carbonate. The eluent used for the non-suppressed IC system contained 0.1 M boric acid and 1.9 mM tartaric acid adjusted to pH 4.5 with the addition of sodium hydroxide solution. The eluent for sodium determination contained 0.5 M EDTA and 2 mM nitric acid. The electrolyte for CE contained 5 mM sodium chromate and 0.5 mM Waters CIA-Pak OFM anion-BT at pH 8.0.

Standard stock solutions of inorganic anions were prepared by dissolving appropriate amounts of the sodium salts in water. Working solutions of these ions were obtained by diluting the stock solutions with sodium hydroxide to give a final concentration of 1 M NaOH. The inorganic anions in the final sample solution were fluoride (3 μg/ml), chloride (3 μg/ml), nitrite (6 μg/ml), bromide (6 μg/ml), nitrate (6 μg/ml), sulfate (8 μg/ml) and phosphate (10 μg/ml).

The hydrogen ion donating medium used in the anode compartment was a slurry of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200-400 mesh in 1 mM octanesulfonic acid (2:1, w/v). The cathode compartment was filled with 0.1 M sodium hydroxide. Octanesulfonic acid solution was prepared by passing a solution of sodium octanesulfonate through a glass column packed with 100 g of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200-400 mesh. The cation-exchange resin was washed thoroughly with Milli-Q water prior to use. The cation-exchange membranes used in this work were obtained from Tokuyama Soda Company, Japan (Neosepta CM-2 and CMS) and Asahi Glass Company, Japan (CMV).

7.2.4 PROCEDURES

7.2.4.1 Optimization of the design of the flow-through electrodialysis device

A solution of 1 M NaOH containing a mixture of inorganic anions in the concentration range 3-10 µg/ml was passed through the sample compartment at a constant flow-rate of 0.1 ml/min using a syringe pump (Razel Sci. Inst., Inc., Stamford, USA), whilst a DC potential was applied at constant power (2 W) to the electrodes at the two ends of the cell. The outlet of the sample compartment was connected to a six-port switching valve fitted with a standard 20 µl sample loop so that direct injection of the neutralized sample solution onto a suppressed IC system was possible. The hardware configuration of this system is shown schematically in Fig. 7.2.

7.2.4.2 Determination of fluoride in forage vegetation samples obtained from the vicinity of an aluminium smelter

Vegetation samples for this work were obtained from Tomago Aluminium, New South Wales, Australia and these samples were prepared and neutralized by the following procedure:

1. Approximately 2.0 g of ground dried sample was weighed into a nickel crucible and 10 ml of 5 g/l calcium oxide was added to form a slurry.
2. The crucible was placed on a hotplate, charred for 1 h and transferred to a muffle furnace at 600^0 C for 2 h.
3. 3.0 g of sodium hydroxide pellets were added and fused for 3 min at 600^0 C.
4. The crucible was removed from the furnace and carefully swirled to suspend the particulate matter until the melt solidified.
5. After cooling, the fused sample was dissolved and diluted with Milli-Q water in a 100 ml volumetric flask to give a final hydroxide concentration of 0.75 M.

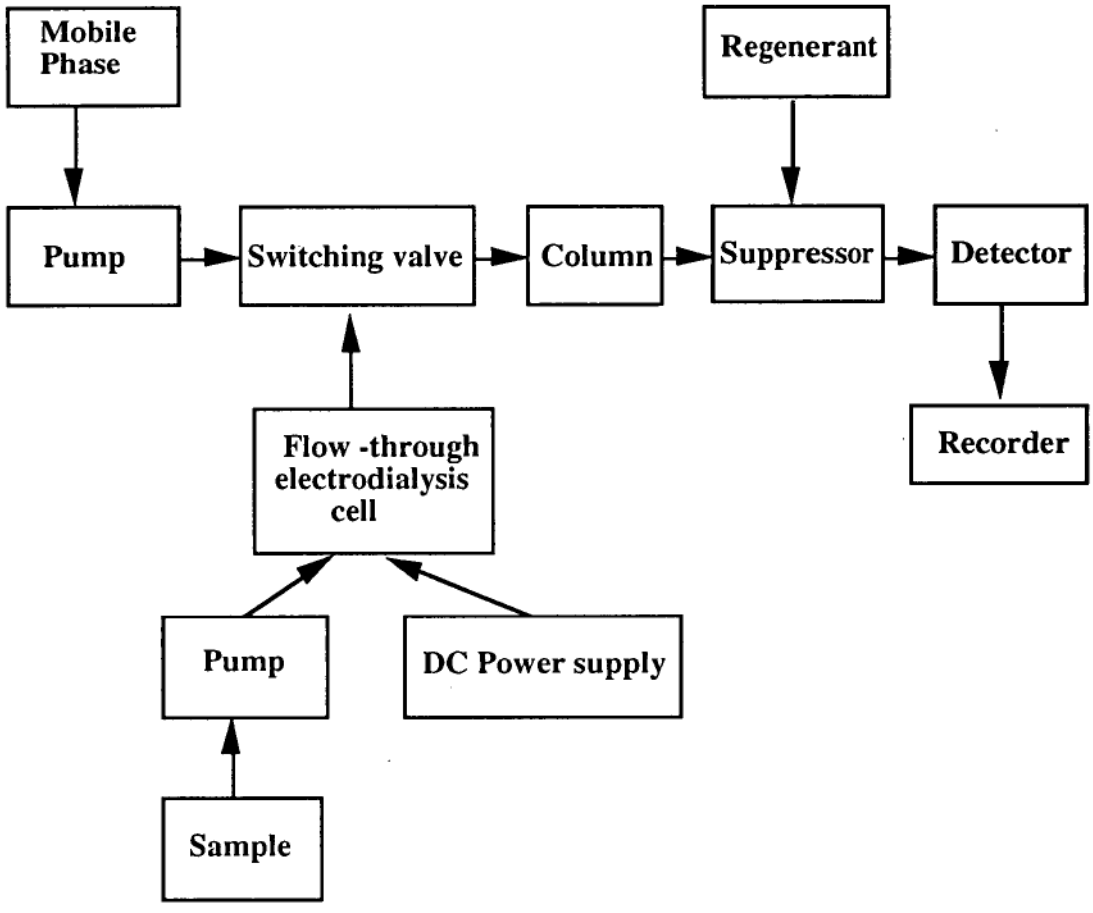

Fig. 7.2 Instrumentation for on-line electrodialysis coupled with suppressed ion chromatography.

6. The hydroxide solution was neutralized using the flow-through electrodialysis device using the conditions described earlier.
7. The concentration of fluoride present in the sample was determined by IC and the results were compared with those obtained by colorimetry (the colorimetric results were provided by Tomago Aluminium).

7.2.4.3 Determination of fluoride and sulfate in dust samples obtained from an aluminium smelter

The dust samples were obtained from Comalco Aluminium, Tasmania, Australia and the solutions were prepared and neutralized as follows :

1. Approximately 0.2 g of sample was weighed into a nickel crucible, 3.0 g of sodium hydroxide pellets was added and the mixture was fused for 10 min at 800^0 C.
2. The same amount of sample was weighed into a nickel crucible and fused with 2.0 g of sodium carbonate at 800^0 C for 30 min.
3. The crucible was removed from the furnace and after cooling, the hydroxide fused sample was dissolved and diluted with 20 mM tartaric acid in a 100 ml volumetric flask to give a final hydroxide concentration of 0.75 M, whilst the carbonate fused sample was dissolved and diluted to 100 ml with Milli-Q water.
4. The hydroxide sample solution was neutralized using the flow-through electrodialysis device and the concentrations of fluoride and sulfate present were determined by IC.
5. The fluoride and sulfate present in the hydroxide sample solution and in the carbonate sample solution were determined by CE after 10-fold dilution in Milli-Q water.

7.3 RESULTS AND DISCUSSION

7.3.1 DESIGN OF THE FLOW-THROUGH ELECTRODIALYSIS DEVICE

The first goal of this work was the design and construction of a flow-through cell suitable for the neutralization of strongly alkaline solutions, while at the same time allowing the cell to be connected directly to an IC system. The cell requires compartments for housing the sample, the hydrogen ion donating medium (anode compartment) and the receiver (cathode compartment). This configuration was obtained by modifying the three-compartment cell used in Chapter 6 to include a sample compartment made by cutting a flow-path into a perspex disc, both sides of which were covered by planar cation-exchange membranes. The upper part of the perspex disc was drilled and threaded to make an inlet and outlet so that the sample was able to flow during the electrodialysis process. Three types of sample compartments were made, as shown in Fig. 7.3. The electrode compartment was constructed by machining a chamber in the centre of a perspex block. Several holes were drilled from the upper section of the perspex block for introducing the electrode and the required solution into the compartment. Previous electrodialysis work had shown that the membrane requires mechanical support to prevent distortion after prolonged use due to heat generated inside the cell. This mechanical support in the static electrodialysis cell was provided by holding the membrane between two perspex discs through which had been drilled numerous holes. In the flow-through cell, support for the membrane was provided by a similar perforated perspex sheet which formed one wall of the electrode chamber. The components of the cell were held together with longitudinal screws, to form the flow-through electrodialysis cell shown in Fig. 7.1.

Previous work had demonstrated that the neutralization process could be achieved by applying either constant current or constant power. Preliminary tests on the flow-through cell using sample compartment 1 (shown in Fig. 7.3), a Neosepta CM-2

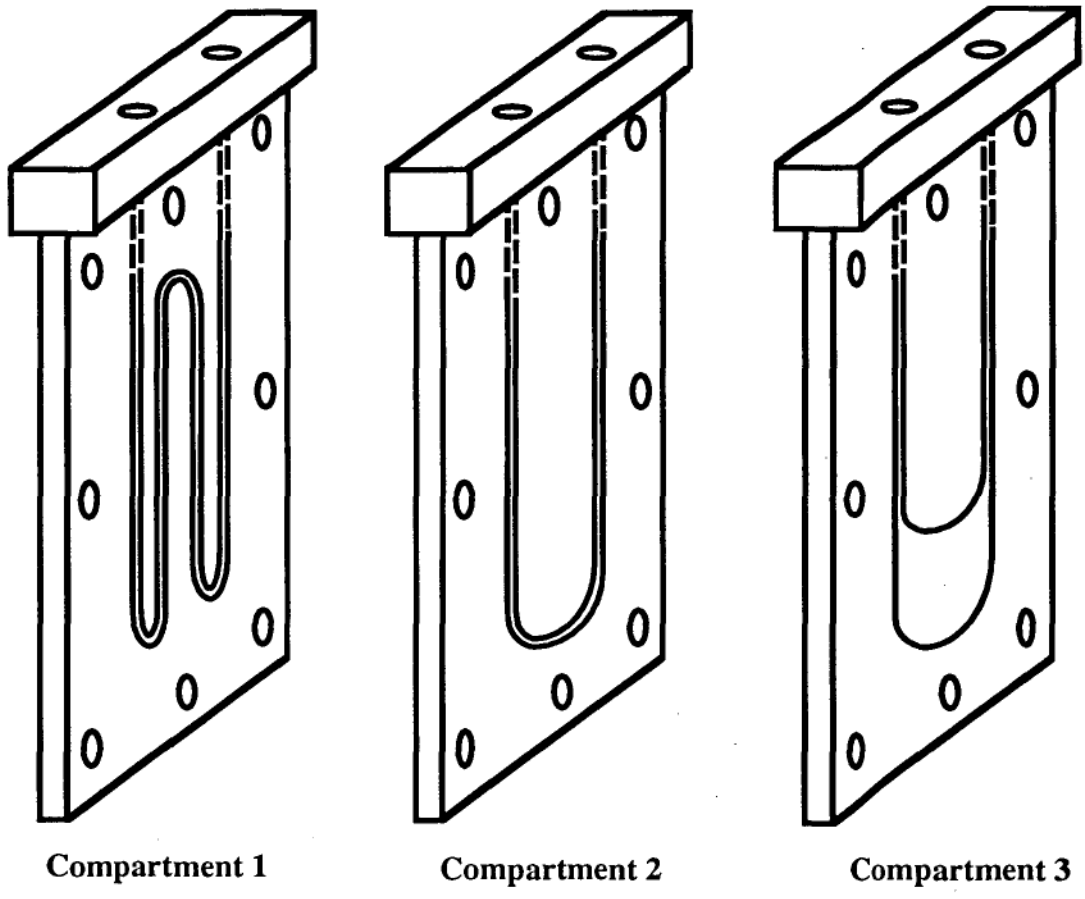

Fig. 7.3 Sample compartments constructed for the flow-through electrodialysis cell.

cation-exchange membrane and platinum wire electrodes (50 x 0.2 mm OD) showed that constant current in the range of 110-130 mA was required to neutralize a solution of 1 M NaOH at a flow rate of 0.1 ml/min. Similarly, a constant power of 4 W was required to neutralize the same sample solution. Further studies showed that 1 M NaOH could be neutralized at a higher sample flow-rate by applying a greater constant current or power, but this also caused the sample solution to heat up which ultimately distorted the membranes. Fig. 7.4 shows the current required for neutralization at different sample flow-rates.

Constant currents of 110 mA, 120 mA and 130 mA were used to evaluate the mechanical stability of the Neosepta CM-2 membrane in conjunction with studies on the recovery of inorganic anions from 1 M NaOH solution. In most cases, the final pH of the sample solution was 6 and the recovery values for the inorganic anions are listed in Table 7.1. From the table, it can be seen that the recovery values were generally higher at lower applied current. For this reason, the lower current was preferred initially for the electrodialysis process, but it was found that the most consistent results were obtained when 120 mA was used as the applied current.

Under the experimental conditions described above, a considerable amount of heat was generated inside the flow-through cell after several cycles of sample neutralization, resulting in pronounced buckling of the membranes. Increasing the total conductivity of the cell by addition of cation-exchange resin beads (AG 50W-X8, H^+ form, 200-400 mesh) to the sample gallery was attempted. However, the resin beads actually caused heat production to increase. A possible cause was the transformation of the resin into its sodium form when contacted by the sodium hydroxide sample solution in the sample chamber, with a resultant increase in resistance.

Two different sample compartments (as shown in Fig. 7.3) were constructed in addition to the first sample compartment and these were evaluated as a means to

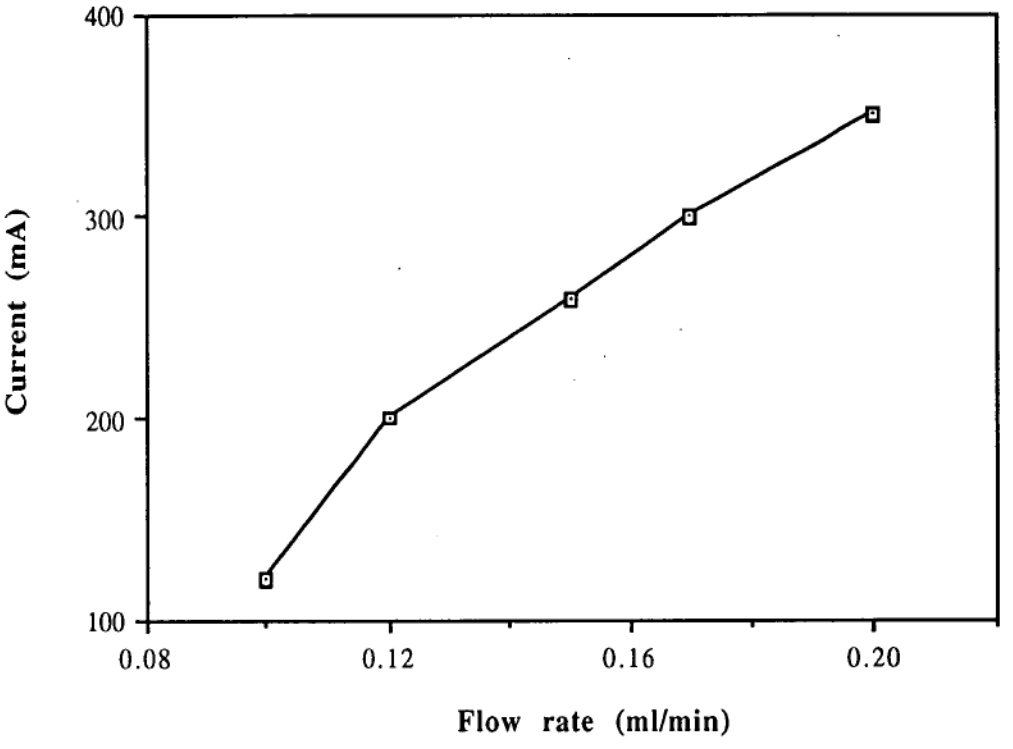

Fig. 7.4 Constant current required for the neutralization of 1 M NaOH using the flow-through electrodialysis cell at different flow-rates.

TABLE 7.1
PERCENTAGE RECOVERY OF ANIONS (IN THE RANGE OF 3-10 μg/ml) FROM 1 M NaOH SOLUTION AFTER ELECTRODIALYSIS WITH NEOSEPTA CM-2 MEMBRANE USING VARIOUS VALUES OF APPLIED CURRENT.
The range derived from 5 replicates is shown in parentheses.

Current	F^-	Cl^-	Br^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}
130 mA	71.8 (6.7)	93.5 (5.3)	84.4 (9.3)	82.6 (4.8)	82.5 (6.8)	83.0 (8.3)
120 mA	75.6 (5.8)	95.0 (4.6)	81.4 (8.6)	87.8 (7.2)	85.2 (7.0)	89.6 (6.7)
110 mA	76.9 (9.2)	94.5 (6.2)	86.0 (9.2)	92.4 (5.4)	89.6 (8.0)	93.2 (5.2)

reduce the heat generated inside the cell. Despite differences in the accommodated sample volume (290 µl, 155 µl and 300 µl for compartments 1, 2 and 3, respectively, in Fig. 7.3), the thickness and the contact area of the flow gallery, all compartments required approximate currents of 120 mA for the neutralization of 1 M NaOH sample solution. However, the sample compartments showed different resistance, as indicated by the differences in power and potential when a constant current of 120 mA was applied to each of the three sample compartments. These differences are listed in Table 7.2. After several neutralization experiments, highly distorted membranes resulted for the cell with compartment 2 (155 µl) and some degree of burning could be noticed. Less pronounced buckling was obtained using compartment 3 (300 µl) which had the greatest contact area to the solution. This compartment was therefore used in further studies. The above result suggests that the contact area between the membrane and the sample solution was an important factor during the process.

7.3.2 SELECTION OF ELECTRODE SIZE

Although the use of the sample compartment 3 reduced heat production inside the cell, continuous use of the cell led to a gradual increase in the temperature of the solutions in the electrode compartments. The resistance of the cell was therefore still high. Another factor that influences the resistance is the size of the electrodes. It is known that the resistance of a solution between two electrodes of a cell is inversely proportional to the area of the electrodes [2]. For this reason, various electrodes with different surface areas were evaluated in an effort to decrease the cell resistance. This study was carried out using the static electrodialysis cell employed in the previous studies under conditions of varying applied power. The results obtained are shown in Table 7.3, from which it can be seen that stainless steel plate electrodes 12 mm wide generated the highest current at lowest potential when constant power was applied to the cell. Increasing the size of the electrode to 15 mm gave no significant change in performance.

TABLE 7.2
POWER (W) AND POTENTIAL (V) GENERATED BY APPLYING A CONSTANT CURRENT OF 120 mA USING DIFFERENT SAMPLE COMPARTMENTS.

Sample	Dimension (mm)			Volume (µl)	Power (W)	Potential (V)
compartment*	Length	Thickness	Width			
1	155	1.1	1.7	290	4	33
2	70	1.3	1.7	155	6	50
3	n.a.	1.3	n.a.	300	3	25

n.a. = not available.

* = see Fig. 7.3

TABLE 7.3
COMPARISON OF CURRENT (mA) AND POTENTIAL (V) FOR DIFFERENT ELECTRODES AT VARIOUS VALUES OF APPLIED POWER USING A STATIC ELECTRODIALYSIS CELL.

Power	Width of electrode (mm)						
	0.2 OD*	0.3 OD*	3.0#	6.0#	9.0#	12.0#	15.0#
1 W	60 mA	80 mA	105 mA	120 mA	126 mA	135 mA	135 mA
	16 V	12 V	9 V	9 V	8 V	8 V	8 V
2 W	85 mA	116 mA	158 mA	180 mA	185 mA	190 mA	190 mA
	23 V	17 V	12 V	11 V	10 V	10 V	10 V
3 W	115 mA	140 mA	196 mA	226 mA	234 mA	240 mA	240 mA
	26 V	21 V	15 V	13 V	13 V	12 V	12 V
4 W	130 mA	160 mA	224 mA	270 mA	274 mA	285 mA	285 mA
	32 V	25 V	18 V	15 V	14 V	14 V	14 V

* = Platinum wire electrode (50 mm length).

= Stainless steel plate electrode (0.7 mm thickness x 45 mm length).

These results showed that the conductivity of the cell was increased using larger electrodes so that heat production when the cell was used continuously could therefore be reduced. The results also indicated that large electrodes were required to reach the desired current of 120 mA using lower values of applied power in the flow-through cell. The final design of the flow-through cell comprised sample compartment 3 with stainless steel plates (60 x 25 x 0.7 mm) used as electrodes (as shown in Fig. 7.1). Under these conditions, a current of 120 mA was generated when a constant power of 2 W was applied to the cell. These conditions were further evaluated by examining changes in the membranes as well as the heat generated during the continuous neutralization of a sample. The results showed that a constant power of 2 W was satisfactory with no excessive heat being generated after 8 hours of continuous neutralization of 1 M NaOH solution flowing at 0.1 ml/min through the cell. A constant power of 2 W was therefore used for further studies.

7.3.3 SELECTION OF THE MEMBRANE

Previous work using the static cell had shown that the permselectivities of the membranes, assessed by determining the recoveries of a range of inorganic anions initially added to NaOH solution before the samples were subjected to electrodialysis process, played an important role in ensuring the success of the process. Preliminary results for the electrodialysis of a 1 M NaOH solution using the sample compartment 1 with the constant current mode were shown earlier in Table 7.1. This table shows that the three different currents used for the neutralization process gave similar recovery results to those obtained using the static cell, with the exception of fluoride ion. The explanation offered in Chapter 6 for the low recovery of fluoride was that this was due to the diffusion of the protonated fluoride species through the membrane. However, the percentage recovery of fluoride obtained with the flow-through cell was higher than previous results using the same membranes in a static cell. This effect might be expected to be the same

for other weak acid anions, such as nitrite. For this reason, nitrite was included in the sample solution in further studies.

The permselectivity of three different types of membranes (Neosepta CM-2, Neosepta CMS and Asahi CMV) was evaluated using the flow-through electrodialysis cell. A constant power of 2 W (which correlated to a current of 120 mA) was applied to the process and the results are given in Table 7.4. From the table, it can be seen that low recoveries of nitrite were obtained using all three membranes. This suggested that the permselectivity of these membranes toward nitrite were insufficient, presumably due to formation of protonated nitrite species and diffusion of this neutral species from the sample compartment. However, the formation of nitrate in the neutralized solution observed in the static cell was not evident using the flow-through cell. It can also be seen from Table 7.4 that the Neosepta CM-2 membrane gave the best average recovery values for all anions, except for fluoride and nitrite. These values were in accordance with the recovery results obtained using the same membrane in the static electrodialysis cell. The best recovery for fluoride was achieved using the Neosepta CMS membrane, although other anions were not recovered quantitatively. Of the three membranes tested, the Asahi CMV membrane gave the poorest recoveries for all anions.

The ability to successfully treat samples containing fluoride is an improvement over the static cell described in Chapter 6 and is attributable to the fact that loss of fluoride by diffusion of hydrogen fluoride through the membrane does not occur, since this species is formed only when the sample is about to exit the cell. Chromatograms showing a mixture of inorganic anions in Milli-Q water and in 1 M NaOH after electrodialytic treatment using the Neosepta CM-2 membrane are given in Fig. 7.5. The two chromatograms are virtually identical, except for the low recovery of fluoride and nitrite in the treated sample.

TABLE 7.4
PERCENTAGE RECOVERY OF ANIONS (PRESENT IN THE RANGE 3-10 μg/ml) FROM 1 M NaOH SOLUTION AFTER ELECTRODIALYSIS AT 2 W USING VARIOUS CATION-EXCHANGE MEMBRANES IN THE FLOW-THROUGH CELL.
The range derived from 8 replicates is shown in parentheses.

Anions	Membrane		
	Neosepta CM-2	Neosepta CMS	Asahi CMV
F^-	84.3 (3.5)	95.8 (3.0)	73.4 (5.2)
Cl^-	99.2 (2.1)	89.0 (4.8)	84.7 (4.2)
NO_2^-	53.0 (4.2)	53.3 (2.6)	48.4 (3.8)
Br^-	94.6 (2.5)	92.5 (3.5)	72.5 (2.7)
NO_3^-	98.4 (3.0)	88.5 (5.3)	74.5 (6.1)
HPO_4^{2-}	99.6 (1.0)	93.2 (4.5)	84.6 (3.4)
SO_4^{2-}	98.5 (2.4)	94.0 (5.2)	85.2 (5.0)

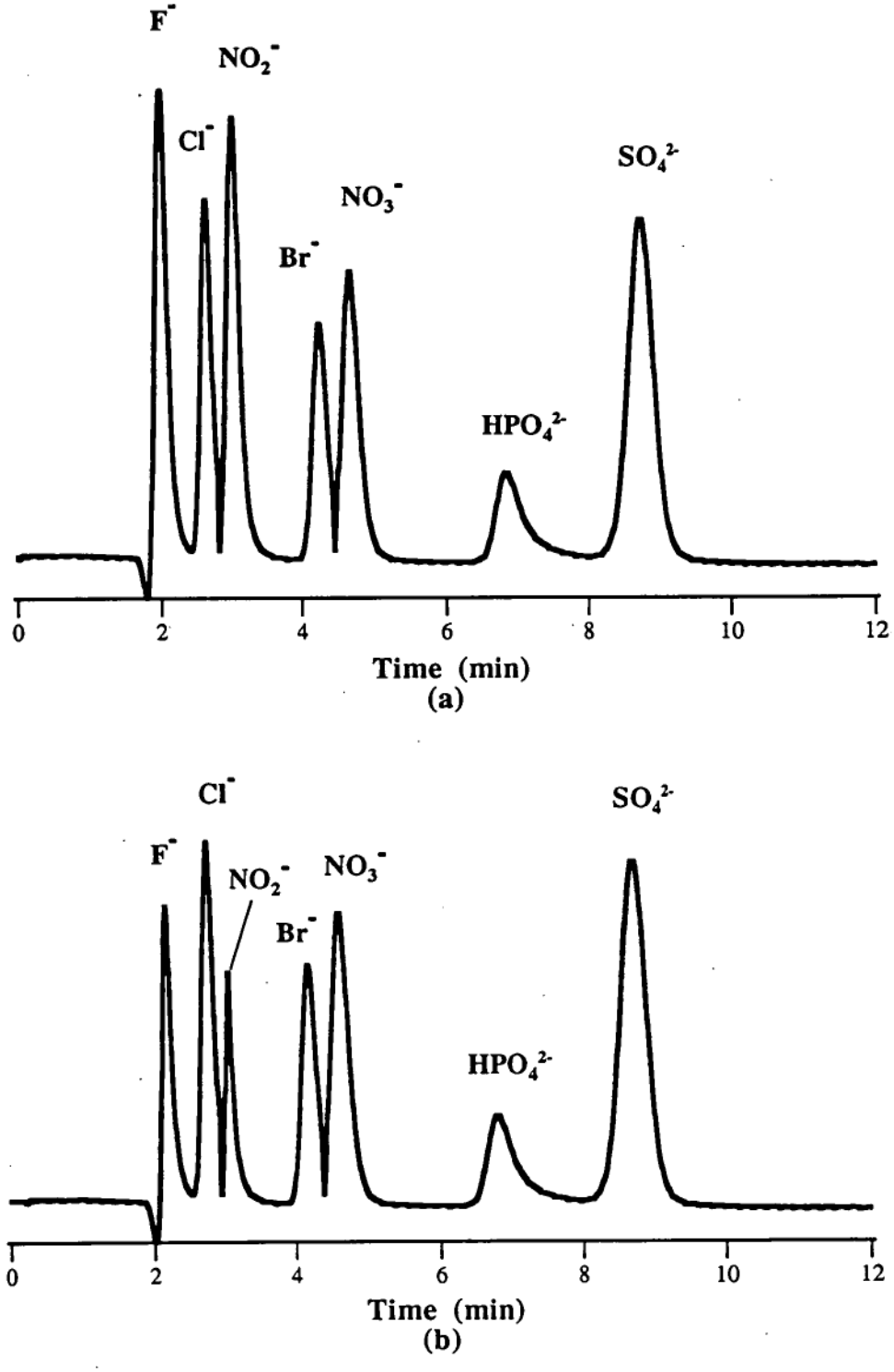

Fig. 7.5 Chromatograms of inorganic anions (3-10 µg/ml) in (a) Milli-Q water and (b) 1 M NaOH after electrodialytic treatment using Neosepta CM-2 membranes. Injection volume : 20 µl. Eluent : 2.0 mM Na_2CO_3 - 2.0 mM $NaHCO_3$. Column : Dionex HPIC-AS4A with AG4A Guard Column and AMMS Suppressor.

7.3.4 ELECTRODIALYSIS OF OTHER ALKALINE SOLUTIONS

Dissolution of samples which are not readily soluble in water can often be accomplished by alkaline fusion technique. This technique includes fusion of the sample with common alkalis, such as sodium hydroxide, sodium carbonate and sodium tetraborate. Several papers have reported on the use of this method for sample preparation in IC for samples such as glass [3], insoluble waste-water precipitate [4] and rock materials [5]. Neutralization and dilution of the fused sample solution usually follow the dissolution procedure before the IC determination can be performed. However, these steps will frequently create problems in the final chromatogram. A high level of the acid anion resulting from the neutralization step may obscure the peaks of other anions, whilst dilution may result in the concentration of trace analyte species reaching the instrumental detection limit.

The electrodialysis techniques described in this thesis have been designed to handle this type of sample without alteration in the concentration of the analyte of interest. The method has performed successfully in the neutralization of sodium hydroxide solutions. The electrodialysis process is now applied to the neutralization of sodium carbonate and sodium tetraborate solutions in order to determine the utility of the method for samples fused using these materials.

Neutralization of 1 M, 0.5 M and 0.2 M Na_2CO_3 solutions was carried out at varying values of constant applied power using the flow-through cell. The pH of these solutions after the electrodialytic treatment are shown in Table 7.5. From the table, it can be seen that the lowest pH reached for the electrodialysate was approximately 7. This can be attributed to the fact that partial replacement of sodium ions in the sample with hydrogen ions leads to the formation of bicarbonate, which in turn dissociates partially to resist total replacement of sodium ions. This results in the pH of the solution remaining higher than 7 in some cases.

TABLE 7.5
pH OF 1 M (pH=13), 0.5 M (pH=12) AND 0.2 M (pH=11) Na_2CO_3 SOLUTIONS AFTER ELECTRODIALYSIS USING THE FLOW-THROUGH CELL AT VARIOUS VALUES OF APPLIED POWER.

	Na_2CO_3 [M]		
Power	1.0	0.5	0.2
2 W	9.0	8.5	8.0
3 W	9.0	8.0	7.5
4 W	8.5	7.5	7.0
5 W	8.0	7.0	7.0

The following equilibrium illustrates this phenomenon.

$$CO_3^{2-} + H^+ \leftrightharpoons HCO_3^- \quad K_1 = 5.6 \times 10^{-11}$$
$$HCO_3^- + H^+ \leftrightharpoons H_2CO_3 \quad K_2 = 4.3 \times 10^{-7}$$

The partial replacement of sodium ion and the resultant high concentration of carbonate and bicarbonate in the final solution caused saturation of the suppressor system when the electrodialysed sample was analysed by suppressed IC mode. This resulted in severe baseline distortions in the chromatogram. This effect is shown in Fig. 7.6 (a) where the bicarbonate peak obscured the early eluted anions, especially fluoride and chloride. The use of the static electrodialysis cell to neutralize the sodium carbonate solution was also examined. The results showed that neutralization could not be achieved, since the release of carbon dioxide from the sample solution during electrodialysis caused extensive loss of sample solution through aerosol formation. Unless some modification to the design of the sample compartment was made, neutralization of sodium carbonate solutions could not be achieved.

The neutralization of sodium tetraborate solutions was also carried out using the flow-through electrodialysis cell. The concentration of sodium tetraborate that could be neutralized using this technique was limited by its solubility in water. A maximum concentration of 0.1 M was obtained and neutralization of this solution was achieved by reducing the pH from 9.5 to 6. However, a chromatogram of the neutralized solution (shown in Fig. 7.6 (b)) showed severe distortion due to boric acid which completely obscured peaks of inorganic anions in the sample solution.

The displacement efficiency of the electrodialysis technique, which usually governs the capacity of the neutralization process, was examined by determining the concentration of residual sodium in the electrodialysed solutions. This was determined on samples of sodium hydroxide, sodium carbonate and sodium tetraborate using an IC method and the results are shown in Table 7.6.

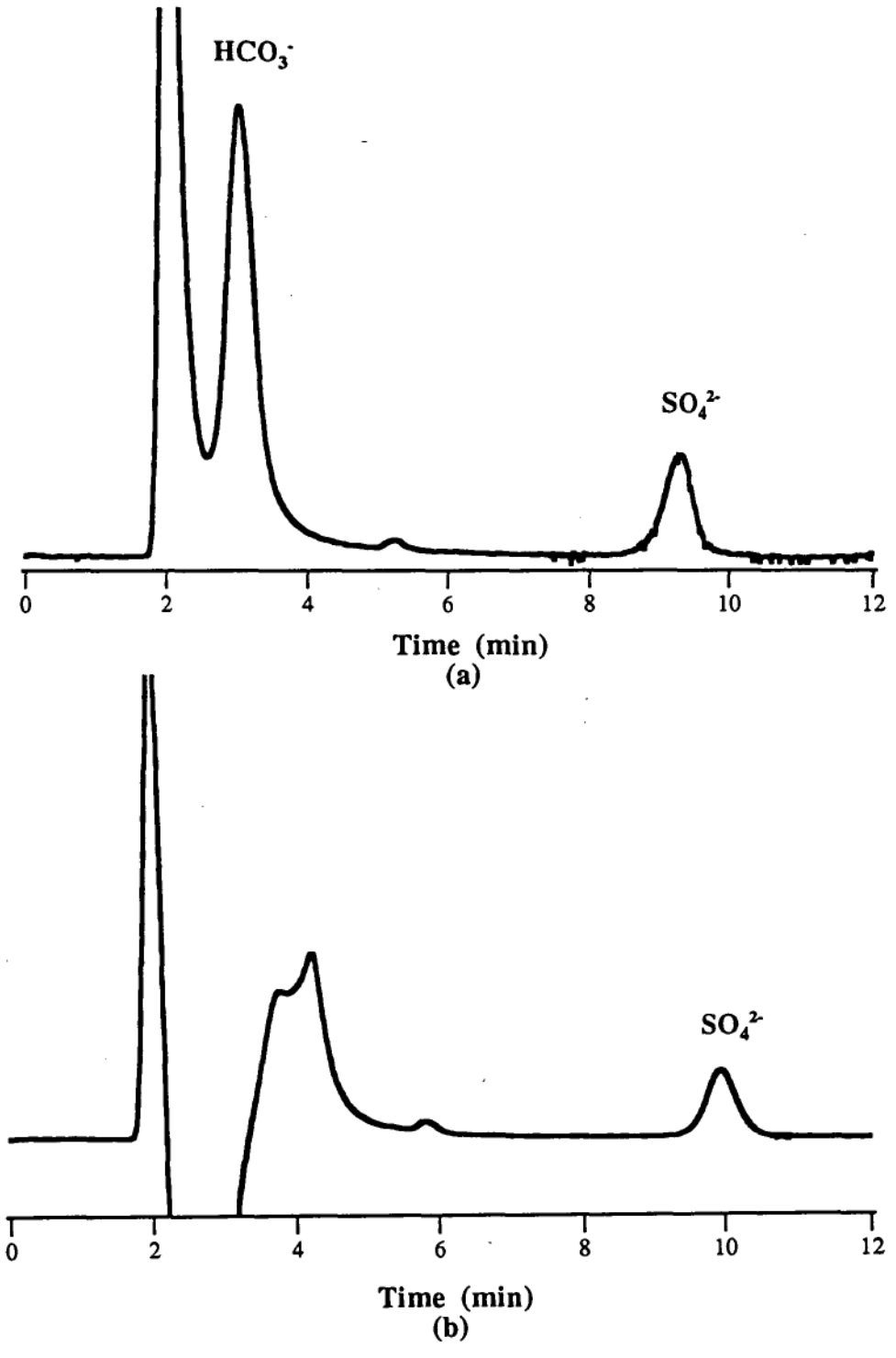

Fig. 7.6 Chromatograms of (a) 1 M Na_2CO_3 solution and (b) 0.1 M $Na_2B_4O_7$ after electrodialytic treatment using the flow-through electrodialysis cell. Injection volume : 20 µl. Eluent : 2.0 mM Na_2CO_3 - 2.0 mM $NaHCO_3$. Column : Dionex HPIC-AS4A with AG4A Guard Column and AMMS Suppressor.

TABLE 7.6
RESIDUAL SODIUM PRESENT IN VARIOUS ALKALINE SOLUTIONS AFTER ELECTRODIALYTIC TREATMENT.
The range derived from 5 replicates is shown in parentheses.

Solution	Na^+ in original solution (μg/ml)	Na^+ in dialysed solution (μg/ml)	Displacement efficiency (%)
1 M NaOH	23000	108 (56)	99.5 (0.2)
1 M Na_2CO_3	46000	20500 (700)	55.4 (0.5)
0.5 M Na_2CO_3	23000	2250 (65)	90.2 (0.3)
0.2 M Na_2CO_3	9200	216 (42)	97.7 (0.5)
0.1 M $Na_2B_4O_7.10H_2O$	4600	28 (8)	99.4 (0.2)

A displacement efficiency of 99.5% was obtained for the dialysed 1 M sodium hydroxide solution, which indicated that most of sodium ions in the solution were replaced by hydrogen ions. A similar figure was obtained for the dialysed solution of 0.1 M sodium borate. On the other hand, sodium ions in the dialysed solution of 1 M sodium carbonate were only partly displaced with hydrogen ions and therefore the final pH of this solution was about 9. The residual sodium in 0.2 M sodium carbonate solution after dialysis was about 20 times greater than for a more concentrated sodium hydroxide solution.

The results obtained for the neutralization of sodium carbonate and sodium tetraborate solutions indicate that the flow-through cell was unsuitable for the treatment of samples fused with these materials. On the other hand, results obtained for sodium hydroxide solutions were promising.

7.3.5 APPLICATIONS

The feasibility of using the electrodialysis technique as a simple and rapid sample pretreatment method was investigated by using the flow-through electrodialysis device coupled on-line with IC to determine anions in samples of interest in the aluminium industry following sample preparation by hydroxide fusion.

7.3.5.1 Determination of fluoride in forage vegetation samples obtained from the vicinity of an aluminium smelter

Fluoride is a major environmental pollutant from an aluminium smelter and it can be absorbed and accumulated in the tissues of plants which grow in the vicinity of an aluminium smelter. Whilst there is no standardised method yet for sample preparation prior to fluoride analysis, acid leaching and hydroxide fusion are the

most commonly employed techniques. These processes are frequently followed by distillation and colorimetric determination after reaction with alizarin fluorine blue-lanthanum reagent [6]. Other determination procedures, such as potentiometry [7-9], have also been reported.

When the analyte of interest, such as fluoride, is present in a highly alkaline matrix, the IC approach favoured for limited sample preparation is usually ion-exclusion chromatography [10], since ion-exclusion columns are tolerant of samples having a high ionic strength. However, problems associated with the use of ion-exclusion chromatography for the determination of fluoride in vegetation samples after hydroxide fusion have been reported recently [11]. It was noticed that this approach had a disadvantage in that elevated levels of silica present in the samples resulted in a build-up of silica on the column, reducing column performance. An ion-exchange separation approach combined with solid-phase reagent conductivity detection, following dilution and neutralization steps using hydrogen ion cartridges, was ultimately used in this paper.

In the present work, vegetation samples obtained from the vicinity of an aluminium smelter were prepared by hydroxide fusion as described in the experimental section. The alkaline sample solution was neutralized using the flow-through electrodialysis cell utilizing Neosepta CMS membranes and the cell was connected to a suppressed IC system. The system is shown schematically in Fig. 7.2. The flow-rate of the sample through the cell was 0.1 ml/min and a constant power of 2 W was applied for the neutralization process. The results obtained by IC were compared with those obtained by colorimetry following sample preparation by hydroxide fusion, as shown in Table 7.7. The fluoride content is expressed in mg of fluoride present in 1 g of dried sample and the range from 5 replicates using the electrodialysis treatment is given in parentheses for the IC results.

TABLE 7.7
COMPARATIVE RESULTS FOR FLUORIDE CONCENTRATION IN VEGETATION SAMPLES.

Sample	Ion chromatography (µg/g)	Colorimetry (µg/g)
Vegetation 1	155.6 (3.3)	135
Vegetation 2	554.4 (12.1)	560
Vegetation 3	7.6 (1.0)	7
Standard vegetation	105.5 (3.7)	110
Standard timothy grass 1	68.1 (1.6)	64
Standard timothy grass 2	268.8 (9.1)	277

Two standard reference materials of powdered timothy grass were also included as sample materials. The fluoride content of these standard materials had been determined using various methods, such as titration with thorium nitrate following fusion and distillation, colorimetry following fusion and microdistillation from sulfuric acid, and ion-selective electrode measurement after oxygen bomb decomposition [12, 13].

It has been suggested that the colorimetric measurement, with on-line distillation, determines the "total" fluoride while IC determines only "free" fluoride in the hydroxide fused sample [11], hence some difference between the results may be anticipated. However, the data in Table 7.7 show good correlation between the two methods and this suggests that most of the fluoride present in these types of samples is free fluoride.

The chromatogram of the electrodialysed sample solution using suppressed IC with a carbonate/bicarbonate eluent is shown in Fig. 7.7. The fluoride present in the sample is well resolved from other anions and can be quantitated readily. It was also noticed that there was no interference from the elevated level of silica in the fused sample either in the electrodialysis cell or on the chromatography column throughout the analyses. This represents an advantage in using the electrodialysis cell over the hydrogen ion cartridges. A simple and relatively rapid determination of fluoride was achieved by coupling the flow-through electrodialysis cell with a switching valve.

The feasibility of employing non-suppressed IC for the determination of fluoride in the electrodialysed sample solution was also investigated. As mentioned earlier in Chapter 6, the presence of carbonate (from CO_2) in the neutralized solution interfered with the determination of early eluted anions, such as fluoride and chloride, when non-suppressed IC was employed. It has been reported that carbonate interference can be overcome by the use of tartrate/borate eluents

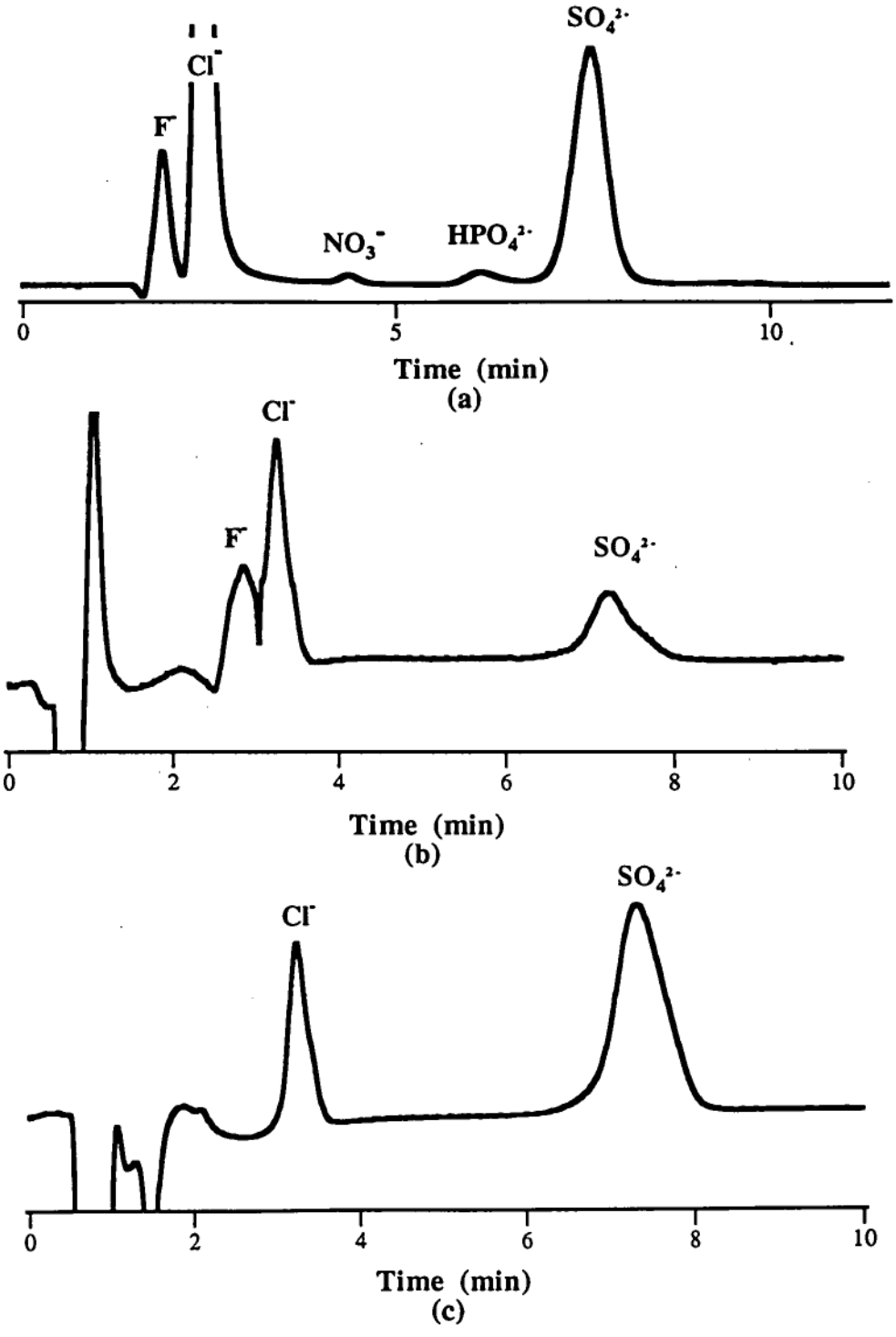

Fig. 7.7 Chromatograms of (a) electrodialysed vegetation sample using suppressed IC mode (column : Dionex HPIC-AS4A with AG4A guard column and AMMS suppressor, eluent : 2.0 mM Na_2CO_3-2.0 mM $NaHCO_3$, injection volume : 20 µl), (b) Mixture of fluoride (50 µg/ml), chloride (10 µg/ml) and sulfate (10 µg/ml) in Milli-Q water and (c) electrodialysed vegetation sample using non-suppressed IC (column : Waters IC Pak anion HR, eluent : 0.1 M boric acid-1.9 mM tartaric acid adjusted to pH 4.5, injection volume : 20 µl).

operated in the pH range 3-5 [14, 15]. At this pH, the carbonate is completely protonated to give neutral H_2CO_3 and is therefore eluted at the void volume.

However, some complications arose in the use of tartarate/borate eluents when applied to the determination of anions that are weakly retained on an anion-exchange resin, such as fluoride. A dilute eluent (i.e. a mixture of 0.1 M boric acid and 1.9 mM tartaric acid adjusted to pH 4.5) was necessary to obtain retention for fluoride, with stronger eluents causing the fluoride to be eluted in the void volume. At this eluent strength, detection sensitivity was reduced greatly as a result of the conductance of the eluent and the partial protonation of fluoride. The detection limit of fluoride on a Waters IC Pak HR anion-exchange column using this eluent was approximately 50 μg/ml (based on a 20 μl injection volume), whilst the final concentration of fluoride in the sample solution was in the range 2-12 μg/ml. An increase in the injection volume produced a large void peak which interfered with the fluoride peak. As a result, fluoride in the sample solution was undetectable using this system and unless the amount of sample used for hydroxide fusion was increased, determination of fluoride using the non-suppressed mode was not possible.

Chromatograms for a mixture of anions in Milli-Q water and the neutralized sample obtained with the tartarate/borate eluent are given in Figs. 7. 7 (b) and (c), respectively. It can be seen that fluoride and chloride in the standard mixture are not fully resolved, whilst chloride and sulfate are the major anions detected in the treated sample using this separation mode.

7.3.5.2 Determination of fluoride and sulfate in dust samples obtained from an aluminium smelter

Apart from fluoride, a significant amount of sulfate may also be released into the atmosphere in the form of SO_2 gas during the production of aluminium [1, 16]. Fluoride and SO_2 (as sulfate) are usually determined in dust collected from the working atmosphere and the reduction cell ventilation air and their concentrations have an important influence on the design of gas collection and cleaning equipment.

Considerable interest has been directed toward the determination of these anions and they are typically analysed by traditional wet chemical methods. Special attention has been focussed on the interference of aluminium (Al^{3+}) in the determination of fluoride, and this is usually attributed to the formation of soluble aluminium fluoro-species [8]. The interference of such complex formation can be minimized by (i) isolating the fluoride as a volatile product (e.g. by including a microdistillation step as is the case for some automated fluoride analysers), (ii) chemical removal of aluminium or (iii) decomposition of the AlF_x complexes. The last approach has been widely adopted in conjunction with fluoride ion-selective electrode measurements, since competing ligand species can be conveniently added as a masking agent. Methods reported using this approach include making measurements at high pH in the presence of sodium citrate [17], by complexation with DCTA (diaminocyclohexane-tetraacetic acid) [18] or with Tiron [19], and by masking with EDTA at pH 9.5 [20].

IC has been applied in a number of cases for the determination of fluoride in aluminium industry samples. Direct determination of gaseous and particulate fluoride in air was possible by suppressed IC when the level of aluminium in the sample was low [7, 21]. The presence of AlF_x complexes has been observed to have a detrimental effect on a non-suppressed IC column [8]. The determination of

anions, such as chloride and sulfate, in Bayer liquor has also been described using suppressed [22] and non-suppressed IC systems [11]. The fact that aluminium hydroxide, which is usually present in the Bayer liquor, is very insoluble restricts the choice of eluents to those which are either of very low pH, very high pH or those which keep the alumina soluble through complex formation. An example of the last approach is the dilution of the Bayer liquor sample in dilute tartaric acid, with the anions (e.g. chloride and sulfate) being analysed by non-suppressed IC using tartrate/borate eluent at pH 4.5 [11]. Under these conditions the soluble aluminium-tartrate complex was eluted at the void volume, together with organic acid anions present at the sample, as a result of the low eluent pH and the high boric acid concentration.

In the present work, a tartrate/borate eluent at low pH combined with complex formation of aluminium-tartrate was utilized to analyse fluoride and sulfate in dust collected from the extraction system of an aluminium smelter. This analysis was employed after hydroxide fusion of the sample and dissolution of the fused sample in 20 mM tartaric acid, followed by neutralization of the sample solution using the flow-through electrodialysis device. The conditions for the non-suppressed IC mode used in this analysis were the same as those used for the analysis of fluoride in vegetation samples described earlier. However, the fluoride peak in the dialysed sample was partially obscured by a large peak due to aluminium-tartrate, so that the quantitation of this anion was not possible. Dilution of the dialysed sample solution proved to be not practicable due to the presence of a system peak in the final chromatogram. These results suggest that different aluminium complexing agents as well as different types of IC eluents are necessary for this determination to be carried out successfully. Figs. 7.8 (a) and (b) show chromatograms of the dialysed sample and the diluted sample, respectively. From Fig. 7.8, it can be seen that sulfate is eluted at approximately 8 min and can be quantitated readily. Suppressed IC was also used to analyse the final dialysed solution, but tartaric acid appeared as a large

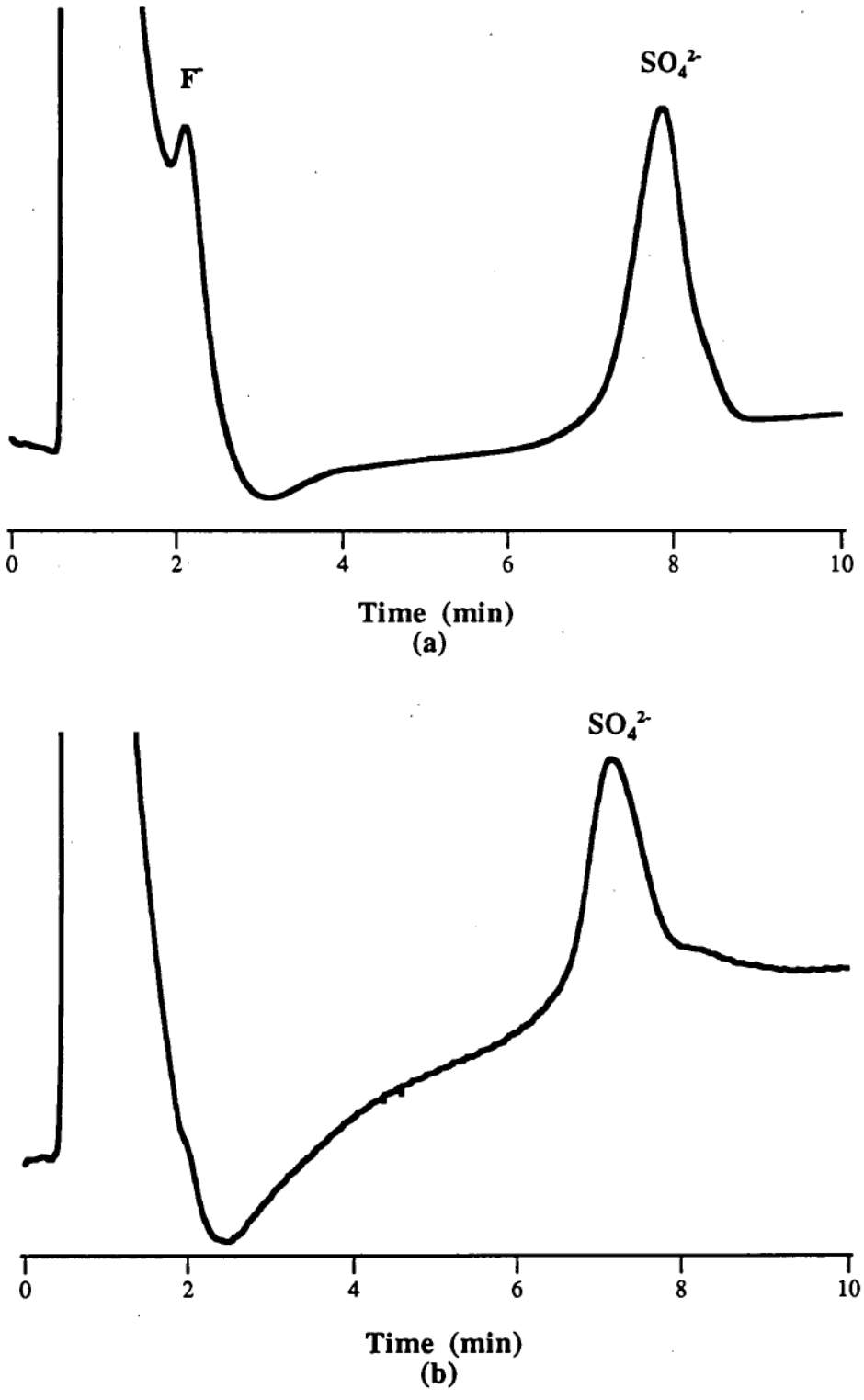

Fig. 7.8 Chromatograms of (a) hydroxide fused dust sample after electrodialysis and (b) the same sample solution after 10-fold dilution in Milli-Q water. Column : Waters IC Pak anion HR. Eluent : 0.1 M boric acid-1.9 mM tartaric acid adjusted to pH 4.5. Injection volume : 20 µl.

peak which interfered with both anions of interest, even after passage of the sample through a C_{18} Sep-Pak cartridge.

The results obtained using the IC measurement coupled with on-line electrodialysis were compared with those for CE. Hydroxide and carbonate fusion were also compared using the CE method to determine the efficacy of the two methods of fusion, since sodium carbonate fusion normally requires a longer time than sodium hydroxide to completely fuse the sample.

Preliminary CE results showed that analysis of the hydroxide fused sample solution (containing tartaric acid to prevent precipitation of alumina during electrodialysis) gave a large peak due to tartaric acid which completely obscured the fluoride. However, the addition of tartaric acid is not essential when the sample is to be analysed by CE, since simple dilution to reduce the hydroxide level proved to be an adequate approach. In this case, direct analysis of the fused sample solutions by CE was carried out after a 10-fold dilution with Milli-Q water. The electrophoregrams for samples fused with hydroxide and carbonate, after 10-fold dilution, are given in Figs. 7.9 (a) and (b), respectively. A comparison of the results obtained by the IC and CE methods is shown in Table 7.8. The concentrations are expressed as mg of anion present in 1 g of dried sample. It can be seen that a slightly higher result for sulfate was obtained by the IC method, but the results obtained for fluoride and sulfate using the two fusion techniques show good correlation. This suggests that the faster hydroxide fusion method could be used as a replacement for the commonly employed carbonate fusion which is much slower.

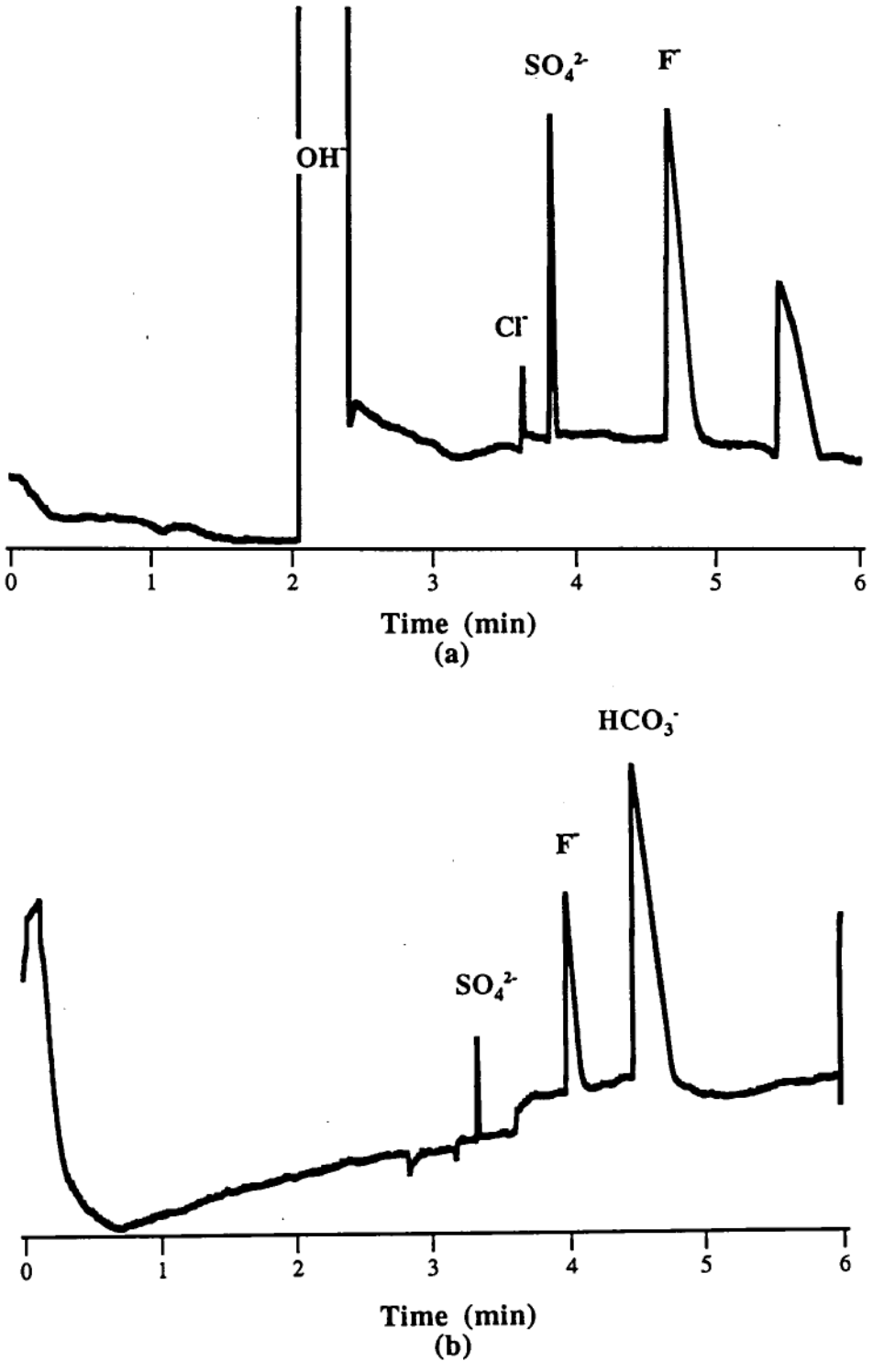

Fig. 7.9 Electropherograms of dust sample (a) fused with sodium hydroxide and (b) fused with sodium carbonate, after 10-fold dilution in Milli-Q water. Capillary : 60 cm x 75 µm ID fused silica. Power supply : negative at 20 kV. Electrolyte : 5 mM chromate, 0.5 mM CIA-Pak OFM anion-BT at pH 8.0. Injection : hydrostatic for 30 sec. Detection : indirect UV at 254 nm.

TABLE 7.8
COMPARATIVE DATA FOR THE ANALYSIS OF FLUORIDE AND SULFATE IN DUST SAMPLES BY ION CHROMATOGRAPHY (IC) AND CAPILLARY ELECTROPHORESIS (CE).

	IC*	CE			
Sample	Sulfate (µg/g)	Fluoride (µg/g)		Sulfate (µg/g)	
	1*	2*	3*	2*	3*
77F	239.6	284.9	296.5	213.3	212.3
79F	223.2	271.6	294.8	206.3	203.4
80F	217.8	287.3	276.7	209.4	201.1
81F	207.8	283.3	308.0	192.5	190.6
82F	186.2	316.9	318.9	176.4	158.9
84F	196.2	235.5	230.0	226.2	227.3

IC* = fluoride could not be quantitated using the IC method.

1* = result obtained by hydroxide fusion and dissolution in 20 mM tartaric acid, followed by electrodialytic treatment.

2* = result obtained by hydroxide fusion and dissolution in Milli-Q water, followed by a 10-fold dilution in Milli-Q water.

3* = result obtained by carbonate fusion and dissolution in Milli-Q water, followed by a 10-fold dilution in Milli-Q water.

7.4 CONCLUSIONS

This study has shown that clean-up of strongly alkaline solutions prior to anion chromatographic analysis can be achieved on-line with the aid of a flow-through electrodialysis device fitted to a six-port switching valve. Optimum performance of the flow-through electrodialysis device was achieved by employing a sample chamber which accommodated 300 µl of sample, using stainless steel plate electrodes (60 x 25 x 0.7 mm), and by passing the sample at a constant flow-rate of 0.1 ml/min through the cell while applying a constant power of 2 W. Under these conditions, 1 M NaOH sample solution could be neutralized in approximately 3 min.

The capability of the electrodialytic treatment to neutralize only sodium hydroxide solutions is considered to be a minor limitation of the technique, since many insoluble solid samples can be dissolved by fusion with sodium hydroxide. The flow-through cell could be used to successfully treat samples containing fluoride without loss when Neosepta CMS membranes are used. This represents an advantage over the static cell. The system was used to determine fluoride and sulfate in samples obtained from an aluminium smelter, following sample preparation by hydroxide fusion.

7.5 REFERENCES

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CHAPTER EIGHT

CONCLUSIONS

This thesis has presented the results of a systematic study of dialysis processes performed with the aid of membrane-based devices, applied as a pretreatment step prior to analysis of alkaline samples by IC. A preliminary study of the utility of an "Elutrap" apparatus for sample enrichment was also undertaken. The pretreatment of alkaline samples was carried out using active (Donnan) dialysis and electrodialysis techniques. A number of experimental parameters were evaluated for ensuring the success of the process. These included design of the membrane-based devices, selection of cation-exchange membranes, types of hydrogen ion donating media and magnitude of applied electrical field for the electrodialysis process. All these factors were investigated with a view to applying dialysis processes to the determination of trace levels of inorganic anions in various matrices following sample preparation by hydroxide fusion.

Donnan dialysis, which was carried out by passing sodium hydroxide solutions containing inorganic anions through a cation-exchange hollow fibre immersed in a hydrogen ion donating medium, proved to be a fast and efficient method for the neutralization of alkaline solutions. The length of the fibre is an important factor to be considered for an effective neutralization process, but performance could be enhanced by employing a fibre packed with polysterenedivinylbenzene beads. Careful choice of the type and concentration of acid solutions used as hydrogen ion donating media is necessary to prevent sample contamination by the acid anion which can penetrate through the membrane during the process. The use of hydrophobic sulfonic acids, such as octanesulfonic acid and camphorsulfonic acid, at a concentration below their penetration threshold (usually 0.1 M) gave best results.

Sample contamination by the acid anion can be avoided when a slurry of BioRad AG 50W-X8 (H^+ form, 200-400 mesh) cation-exchange resin is utilized. The neutralization capacity of the dialysis device was increased greatly when the resin was slurried in 0.1 M octanesulfonic acid, and the maximum theoretical ion-exchange capacity of the resin was attained if the slurry was stirred occasionally. This indicates that the presence of acid solution in the resin slurry is necessary for site-to-site transport of hydrogen ions from the bulk resin to the membrane surface. The Donnan dialysis procedure, under conditions described in this study, is governed largely by the diffusion rate of ions with the result that the concentration of alkali in the sample which can be neutralized by the process is therefore restricted. For this reason, Donnan dialysis is ideal for the neutralization of hydroxide solutions of concentration up to 0.1 M, with no significant loss of the analyte of interest.

The potential applicability of an "Elutrap" device for selective removal of ions from a sample was studied. The migration pattern of inorganic anions under an applied electrical potential was observed to be affected by many factors, such as ionic mobility, ionic size, charge/mass ratio of ion and hydrated radius of ion. However, the membranes used in the device tested were unable to produce either selective removal of anions or sample enrichment.

The limitations of the Donnan dialysis technique in the neutralization of samples having high alkaline concentrations can be overcome by the use of electrodialysis, since the transfer of ions through the membrane is stimulated by the applied electrical field across the membranes. This process was carried out off-line using a three-compartment cell formed by arranging two sheets of cation-exchange membranes in a stack. The cell comprised an anode compartment which contained a hydrogen ion donating medium, a cathode compartment which contained a receiver solution of 0.1 M NaOH, and a sample compartment which contained samples of sodium hydroxide solutions containing trace levels of inorganic anions. The

production of excessive heat inside the cell during the electrodialysis process, which causes distortion of the membrane, has been the major problem in this work. The extent of heat production was reduced greatly by limiting the applied current to 150 mA or the applied power to 3W; under these conditions 1 ml of 1 M NaOH solution could be neutralized in approximately 11 min. The effect of penetration of the acid anion into the sample could be avoided by using a 2:1 (w/v) slurry of BioRad AG 50W-X8 (H^+, 200-400 mesh) cation-exchange resin in 1 mM octanesulfonic acid as the hydrogen ion donating medium. Studies with commercially available cation-exchange membranes showed that the use of the Neosepta CM-2 membrane gave quantitative recoveries of inorganic anions (Cl^-, Br^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}) from 1 M NaOH sample solution. However, poor recoveries of weak acid anions, such as fluoride and nitrite, were obtained by this process. The determination of the concentration of co-ions in the membrane (as a measure of the degree to which a particular anion can diffuse to the membrane) demonstrated that the loss of fluoride and nitrite was due to the formation of their neutral, protonated forms which could then diffuse through the membrane. For this reason, electrodialysis under the conditions used in this study is not recommended for these weak acid anions. The feasibility of employing the electrodialysis process to treat multiple samples simultaneously was also explored and the results suggest that this is possible by arranging the cells in parallel. This does not extend the dialysis time, provided a suitable current or power is applied.

The speed of the electrodialysis process for the pretreatment of alkaline solutions was improved greatly when a flow-through cell, which was developed from the off-line cell discussed above, was employed. The sample compartment was designed to allow the sample to flow during the electrodialysis process and the outlet was connected to a six-port switching valve fitted with a 20 µl sample loop so that direct injection of the neutralized sample solution onto an IC system was possible. Particular attention to the shape of the sample compartment and the size of the

electrodes was essential to optimize the flow-through cell design and to minimize the excessive production of heat inside the cell. Optimal performance was achieved by using a sample compartment which accommodates 300 µl of sample, together with the use of stainless steel plate electrodes (45 x 9 x 0.7 mm). With such a cell, a solution of 1 M NaOH containing a mixture of inorganic anions could be neutralized at a constant flow-rate of 0.1 ml/min and applied constant power of 2 W. Higher applied power enabled a faster sample flow-rate to be used, but also caused the sample solution to heat up. Quantitative recoveries of inorganic anions (Cl^-, Br^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}) in the range 3-10 µg/ml were obtained using a Neosepta CM-2 cation-exchange membrane, whilst quantitative recovery for fluoride could be achieved using a Neosepta CMS cation-exchange membrane. The ability to successfully treat samples containing fluoride is an improvement over the off-line cell and is attributable to the fact that loss of fluoride by diffusion of hydrogen fluoride through the membrane does not occur, since this species is formed only when the sample is about to exit the cell.

The on-line electrodialysis technique has been successfully applied for the IC analysis of inorganic anions in vegetation samples obtained from the vicinity of an aluminium smelter. The analysis was carried out using the flow-through cell, following sample preparation by hydroxide fusion. The results obtained using this technique were in good agreement with those from colorimetric determination. It was also shown that the on-line electrodialysis process offers simplicity and speed for the pretreatment of alkaline samples. This work illustrates that when correctly applied, electrodialysis allows the analysis of samples which have been traditionally difficult to analyse by IC.